**FINAL REPORT—PIT LAKE SYSTEM
CHARACTERIZATION AND REMEDIATION
FOR THE BERKELEY PIT**

**MINE WASTE TECHNOLOGY
PROGRAM ACTIVITY IV, PROJECT 8**

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Foreword

Today, industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources and under mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define and measure the impacts and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the U.S. Department of Energy (DOE) has responsibilities similar to NRMRL in that FETC is one of the several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc., and Montana Tech of The University of Montana (Montana Tech) for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communications link between the researcher and the user community.

The objectives of Activity IV, Project 8 were to characterize several different aspects of the Berkeley Pit lake system to assist in future modeling and remediation plans for this and other pit lakes. The results of this study will help in the future design of treatment processes for cleaning up large acid mine water storage lakes. This experimental test program was conducted at Montana Tech and was directed by Dr. Grant Mitman and Mr. Mark Phillip (Department of Biological Sciences); Dr. Douglas Cameron, Dr. William Chatham, Ms. Licette Hammer, Mr. James Jonas, Mr. Mark Syverson, and Ms. Terri Alley (Department of Chemistry and Geochemistry); and Dr. Courtney Young and Mr. Marty Bennett (Department of Metallurgical Engineering).

Executive Summary

The water chemistry of the Berkeley Pit lake varies with the extent of filling and with the changes in the seasons. The amount of metals precipitated in the surface water layer is dependent on the surface area and climatic changes associated with the four seasons. The Pit lake can be divided into two different sections: the surface water and the deep water. The water chemistry and depth of the surface water is dependent on the season whereas the deep water chemistry is relatively constant throughout the yearly cycle.

Organic compounds in the Berkeley Pit lake water could be the result of fuel spills or leaking fuel or lubrication storage containers (gasoline, diesel fuel, lubricating fluids, etc.) from the days of active mining. A significant amount of machinery was abandoned in the mines prior to their flooding. It is not known if all of the underground fuel and lubricating storage containers (or the contents) for this machinery were removed. Consequently, it is possible that some fraction of the organic carbon in the Pit lake water is from fuel and lubrication materials.

Multiple analyses of water from different locations and depths in the Berkeley Pit have confirmed the presence of organic carbon. The amount of organic carbon as measured by a nondispersive, infrared spectroscopic absorption analysis varies from 3 to 5 parts per million (milligrams of carbon per liter). There is a slight variation of the organic carbon concentration with depth. However, the carbon concentration with depth changed between the fall 1997 and spring 1998 samplings. It is not known if this change is real or an artifact of the analysis methods used.

Sulfate-reducing bacteria (SRB) or SRB activity was undetected in the Berkeley Pit lake system. Earlier reports of SRB activity may have been in error, or possibly metabolically inactive bacteria were isolated by enrichment. Furthermore, the lack of black reducing sediments and poor habitat conditions suggest they may only exist as a refugia or microhabitat population if at all. The researchers involved in this study have not been able to isolate any SRB from the Berkeley Pit lake system. Nevertheless, in our attempt to isolate SRBs, a variety of interesting fungi and yeasts were isolated. Bacteria, although present, were fastidious, and to date, researchers involved with this project have been unable to successfully isolate SRB.

The experimental data demonstrates that ultraviolet (UV) radiation has an effect on the surface waters of the Berkeley Pit lake. Depth profiles for most of the measured parameters (temperature, pH, dissolved oxygen, turbidity, specific conductivity, reduction potential, and the concentration of metals including iron, zinc, aluminum, and copper) were found to be significantly different from those determined for the background experiment in the absence of UV radiation. Profiles for pH helped show that two reactions are at work.

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1. Evaluation of the Water Chemistry, Precipitates, and Sedimentation Rate of the Berkeley Pit Lake

Since remediation of the Berkeley Pit lake will involve either in situ treatment of all the existing water or ex situ treatment of a portion of the water, it is essential to know the water properties with respect to depth. To calculate the logistics for a treatment process, it needed to be determined if the Berkeley Pit was homogeneous or heterogeneous with respect to depth and spatial location. If the Pit lake is heterogeneous, the technology used and the cost associated with ex situ treatment might depend on where the source water is collected. Since the Berkeley Pit is a man-made lake, it would be reasonable to assume it must also have some of the same properties of a natural lake. For example, this might include seasonal changes in the water column.

The Berkeley Pit lake was reported in 1987 as being meromictic or having a density gradient (Ref. 1). At this time, Horseshoe Bend water was still entering the system at 3 to 5 million gallons per day (MGD) with a total calculated inflow of 6 to 8 MGD. Horseshoe Bend water had a lower specific conductivity, i.e., less dissolved solids, than the deeper Berkeley Pit lake water. This set up a situation where the surface water would not undergo a seasonal turnover, i.e., a mixing of the entire body of water, like a natural lake due to the difference in density between the two bodies of water. Levy, et. al.(Ref. 2) studied a smaller pit lake in California (Spenceville Copper Pit) that had been filled for approximately 75 years that showed meromictic conditions, and based on Davis and Ashenberg's (Ref. 1) work, the authors suggested the Berkeley Pit lake might also eventually have the same conditions. The inflows to the Berkeley Pit lake have changed since 1987. Horseshoe Bend water was diverted from entering the Berkeley Pit lake in 1995, and since that time, the only source of water has been groundwater and runoff from the immediate vicinity. Because of

these changes, it was necessary to reevaluate

the Pit lake with respect to depth to determine if the Pit lake can still be classified as being meromictic.

The objective of this portion of the project was to determine if the water chemistry changes with respect to depth in the Berkeley Pit lake system, to determine the major species of the precipitates that create the sediment, and to determine the sedimentation rate associated with the system.

1.1 Methods and Materials

1.1.1 Field Sampling
All field sampling was performed by the Montana Bureau of Mining and Geology (MBMG).

1.1.2 Analytical Methods

1.1.2.1 Metals
Samples used for metals analysis were taken from high-density polyethylene (HDPE) amber bottles that were flushed with argon prior to being filled in the field. For the total recoverable metals, the bottles were preacidified with hydrochloric acid so the final concentration of acid would be 5% (by volume). For dissolved metals, bottles were filled with the raw sample, sealed with no head space, and placed on ice until they could be stored in a refrigerator at the Kelley Lab. For the dissolved metals, the aliquot was filtered through a 0.45-micrometer (Fm) cellulose-acetate filter before it was acidified with spectra-analyzed nitric acid to 2% (by volume).

Both sets of samples were analyzed using an axial view Perkin-Elmer inductively coupled plasma-atomic emissions spectrometer (ICP-AES) equipped with a photodiode array (simultaneously collecting multiple element analysis). U.S.

Environmental Protection Agency (EPA) Method 200.7 was employed for this analysis.

In the November 1997 sample set, both total recoverable metals and dissolved metals were determined for all the samples collected. In May 1998, only dissolved metals were determined for all the sample locations.

1.1.2.2 Anions
Aliquots used for determining the major anion concentrations were also taken from the HDPE amber bottles used for dissolved metals. These were filtered using a 0.45-Fm cellulose-acetate filter before being analyzed.

Anion concentrations were determined using a Dionex ion chromatography column with a conductivity detector. Environmental Protection Agency Method 300.0 was employed for this analysis.

1.1.2.3 Iron Speciation
Aliquots used to determine the total iron and ferrous iron were taken from the total recoverable metals containers. These containers were preacidified with trace-metal-grade hydrochloric acid so the final acid concentration was 5% by volume. The container was then filled with sample and sealed with no head space before it was placed on ice. The samples were analyzed within 48 hours.

Total iron and ferrous iron concentrations were determined using a modified version of Standard Method 3500-Fe D (phenanthroline method).

1.1.2.4 Dissolved Inorganic Carbon
Aliquots were also taken from the HDPE amber bottles used for dissolved metals for the determination of dissolved inorganic carbon. These aliquots were placed in 5-mL glass vials sealed with Parafilm before analysis.

The samples were analyzed for dissolved inorganic carbon (DIC) using a Shimadzu TOC-5000A total organic carbon analyzer. This instrument injects an aliquot of the sample into a phosphoric acid bath (25% by volume), purges the bath with purified air (without carbon dioxide), and determines the DIC concentration with a nondispersive infrared detector.

1.1.2.5 Precipitates
The precipitates were collected from the remainder of the HDPE amber bottles used for the dissolved metals. A 0.45-Fm cellulose acetate filter was used with positive pressure (supplied by argon) to filter the remaining Berkeley Pit lake water samples. The samples were kept cool while filtering to eliminate any precipitation that might occur due to a warming of the sample. The collected precipitates were allowed to air dry for several days in a dessicator.

The precipitates were analyzed using both scanning electron microscopy with an energy dispersive x-ray detector (SEM/EDX) and optical microscopy. The SEM/EDX method was used to determine a semiquantitative elemental analysis of the precipitates and some precipitate morphology. The optical microscopy was used to compliment the SEM/EDX precipitate morphology.

1.2 Results

1.2.1 November 1997 Sample Set
The November 1997 sample set was collected from three different spatial locations on the Berkeley Pit lake over a 2-day period (November 11 and 12). All three locations were sampled at depths of 0.5, 1, 2, 5, 10, 25, 50, and 100 feet. Locations 1 and 2 were additionally sampled at depths of 200 and 300 feet.

1.2.1.1 Field Measurements

The pH of the Berkeley Pit lake water ranged from 3.1 to 3.6 pH units. Locations 1 and 3 showed a slight increase in pH with an increase in depth while Location 2 showed a slight decrease in pH with an increase in depth.

The Specific Conductance (SC) of the Berkeley Pit lake water ranged from 6.1 to 6.8 dS/m after correction to standard temperature (25 °C). The SC was relatively the same in all three locations at the corresponding depths. The upper water (<50 feet deep) had a lower conductivity than the deeper water (>50 feet deep). The upper water ranged from 6.1 to 6.4 dS/m; while the deeper water ranged from 6.7 to 6.9 dS/m.

The temperature of the Berkeley Pit lake water during the time of sampling varied from 4.6 °C to 7.5 °C. Locations 1 and 3 had warmer water near the surface (6.3 °C to 7.5 °C), followed by cooler water between 2 and 25 feet (4.9 °C to 5.4 °C), and finally slightly warmer water below 25 feet (5.6 °C to 6.8 °C). Location 2 had a different temperature depth profile from Location 1 and 3 because the temperature was coldest near the surface (4.8 °C at 0.5 feet) and increased with depth (5.9 °C at 50 feet).

The redox potential (E_H) of the Berkeley Pit lake water varied from 571 to 651 millivolts (mV). All three locations showed a higher E_H in the upper water (<50 feet) ranging from 639 to 651 mV; while the deeper water ranged from 571 to 580 mV.

All three sampling locations had different dissolved oxygen (DO) concentration trends with respect to depth. Location 1 had a slight increase in DO concentration with an increase in depth (2.2 milligrams per liter (mg/L) at 0.5 feet and 3.1 mg/L at 300 feet). Location 2 had a decrease in DO concentration with an increase in depth (12.5 mg/L at 0.5 feet and 1.9 mg/L at 300 feet). Location 3 did not have any trend with respect to

depth (ranged from 2.4 to 5.3 mg/L).

1.2.1.2 Metals Concentrations
In the November 1997 sample set, both total recoverable metals and dissolved metals were determined for each of the sampling locations. Only the major elements will be presented in the text.

1.2.1.3 Total Recoverable Metals
The major and important trace elements were averaged for all of the samples taken. The average, minimum, maximum, and relative standard deviation (RSD) were determined for all of these elements. In Table 1-1 on page 20, the elements with the largest RSDs were arsenic (38.5%), iron (9.5%), boron (10.0%), and potassium (9.4%).

All of the elements shown in Table 1-1 showed a slight decrease in concentration with increasing depth except for iron, arsenic, and potassium. These three elements increased with increasing depth.

1.2.1.4 Dissolved Metals
The major and important trace elements were averaged for all of the samples taken. The average, minimum, maximum, and RSD were determined for these elements (see Table 1-2) The elements with the largest RSDs were: arsenic (39.0%), phosphorous (12.1%), iron (10.3%), and potassium (11.2%).

The same trends in the total recoverable metals were also evident in the dissolved metals. All of the elements showed a decrease in concentration with an increase in depth except for iron, arsenic, and potassium.

1.2.1.5 Anions Concentrations
Anions measurable in the Berkeley Pit lake water (besides metal oxyanions) are sulfate, chloride, and fluoride. The sulfate concentrations were sporadic with respect to depth, although they did tend to

decrease with increasing depth. The sulfate concentrations ranged from 8,000 to 8,700 mg/L SO_4^{2-}. Chloride concentrations were somewhat homogeneous with respect to depth and location. The chloride concentrations ranged from 17 to 23 mg/L chloride$^-$. The fluoride concentrations decreased slightly with an increase in depth at all three locations. The fluoride concentrations ranged from 20 to 25 mg/L fluoride.

1.2.1.6 Iron Concentrations and Speciation

In the method used for this analysis, ferrous iron and total iron were measured, and ferric iron was determined by the difference.

Ferrous iron concentration profiles were nearly the same for all three sampling locations. At depths of 25 feet or less, the ferrous iron concentration was relatively homogeneous (110 to 140 mg/L). At depths greater than 25 feet, the ferrous iron was also homogeneous (825 to 860 mg/L).

At depths of 25 feet or less, the total iron profiles were different for the three locations. At Location 1, the total iron concentration was 890 mg/L at 0.5 feet, then it dropped to 830 mg/L at 1 foot, and finally increased back to 890 mg/L at 2 feet where the concentration remained constant until 25 feet. At Location 2, the total iron concentration was approximately 890 mg/L at 0.5 to 2 feet. From 5 to 10 feet, the total iron concentration dropped to approximately 800 mg/L but increased to 900 mg/L at 25 feet. At Location 3, the total iron concentration was relatively constant from 0.5 to 25 feet (890 to 900 mg/L). Below 25 feet, all three locations had about the same total iron concentration of 1,100 mg/L to a depth of 300 feet.

1.2.1.7 Dissolved Inorganic Carbon

The DIC concentrations were relatively the same for all three sampling locations with respect to depth. At depths of 25 feet or less, the DIC concentration ranged from 2 to 5 mg carbon per liter (C/L). At depths greater than 25 feet, the DIC concentrations were more variable and ranged from 15 to 30 mg C/L.

1.2.1.8 Precipitates

Two different types of precipitates were visible from the samples collected: 1) a filamentous precipitate, and 2) a globular precipitate. Both optical and SEM pictures were taken of both types of precipitates. A semiquantitative analysis was performed on the precipitates using the EDX detector on the SEM.

The filamentous precipitates consisted of primarily calcium and sulfur with trace amounts of iron and silicon. The determined stoichiometry of the filamentous precipitate was: $O_{24}S_{4.2}Ca_{3.6}Fe_{0.1}Si_{0.1}$. These types of precipitates were transparent to translucent under the optical microscope, and they were found in many different sizes ranging from <1-Fm wide by <1-Fm long to 10-Fm wide by 100-Fm long. These precipitates were usually found with a pin-cushion morphology but were also found as single crystals.

The globular precipitates consisted of primarily iron and sulfur with trace amounts of silicon, calcium, aluminum, and potassium. The determined stoichiometry of the globular precipitate was $O_{24}Fe_7S_{2.5}Si_{0.9}Al_{0.2}K_{0.1}$ These types of precipitates were orange to red in color and opaque under the optical microscope, and they were found primarily as agglomerations of smaller precipitates. The singular precipitates were less than 1 Fm^3; however, the agglomerations were as large as 1 mm^3. The agglomerations were mostly composed of the globular precipitates, but sometimes they included the filamentous precipitates as well.

1.2.2 May 1998 Sample Set

The May 1998 sample set was collected from one spatial location, presumably the deepest section of the Pit lake. Samples were collected from this

location over a 4-day period (May 5 to 8). This location was sampled at depths of 0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800, 880, 885, and 888 feet. The sampling was started at the greatest depth and was finished at the surface. Samples were collected from 888 to 800 feet on May 5, 700 to 400 feet on May 6, 300 to 25 feet on May 7, and 20 to 0.5 feet on May 8. The 888-foot depth was believed to be the bottom of the Pit.

1.2.2.1   Field Measurements
The pH of the Berkeley Pit lake water ranged from 2.4 to 2.7 pH units. The pH had a trend of decreasing pH with increasing depth (2.7 pH units at 0.5 feet and 2.5 pH units at 888 feet).

The SC of the Berkeley Pit lake water ranged from 7.6 to 8.1 dS/m after correction to standard temperature. The SC of the water was the lowest at a depth of 0.5 feet (7.6 dS/m) and increased to a depth of 18 feet (8.0 dS/m). From 18 to 888 feet, the SC was relatively constant ranging from 7.9 to 8.1 dS/m.

The temperature of the Berkeley Pit water varied from 4.2 EC to 14.8 EC. The temperature was the warmest at 0.5 feet (14.8 EC), decreased to 4.2 EC at 50 feet, and then slightly increased with increasing depth (6.1 EC at 888 feet).

Berkeley Pit lake water E_H ranged from 619 to 664 mV. The water E_H dropped with an increase in depth. The E_H was relatively constant above 6 feet (661 to 664 mV). From 6 to 100 feet, the E_H dropped (661 mV at 6 feet and 619 mV at 100 feet). Below 100 feet, the E_H was relatively constant (619 to 623 mV).

Berkeley Pit lake water DO concentration ranged from less than 0.1 to 0.4 mg/L. From 0.5 to 4 feet, the DO concentration decreased from 0.2 to <0.1 mg/L. The DO concentration increased

again after 10 feet. From 10 to 888 feet, the DO concentration ranged from <0.1 to 0.4 mg/L.

1.2.2.2   Metals Concentrations
In the May 1998 sample set, only dissolved metals were analyzed. The major and important trace elements were averaged for all of the samples taken. The average, minimum, maximum, and RSD were determined for all of elements in Table 1-3. The three highest RSDs are arsenic (25.0%), phosphorous (9.8%), and potassium (8.2%)

Only iron and arsenic showed an increase in concentration with an increase in depth. The remainder of the elements listed in Table 1-3 showed no change with depth or a slight decrease in concentration with an increase in depth. The iron and arsenic increased in concentration to a depth of 50 feet. Below 50 feet, both had homogeneous concentrations to the bottom of the Pit lake. Although potassium had a large RSD, the concentration was sporadic with respect to depth.

1.2.2.3   Anions Concentrations
The anions present in the Berkeley Pit lake water at measurable concentrations (neglecting metal oxyanions) were sulfate, chloride, and fluoride. The sulfate concentrations were lowest near the surface (8,700 to 9,200 mg/L SO_4^{2-}), relatively constant below 15 to 800 feet (9,100 to 9,200 mg/L SO_4^{2-}), and increased below 800 feet to the bottom (from 9,200 to 9,500 mg/L SO_4^{2-}). The chloride and fluoride concentrations were relatively homogeneous with respect to depth. The chloride concentration ranged from 10 to 16 mg/L, and the fluoride concentration ranged from 31 to 38 mg/L.

1.2.2.4   Iron Concentrations and Speciation
Ferrous iron concentrations increased with increasing depth to approximately 50 feet (240 mg/L at 2 feet to 740 mg/L at 50 feet). Below 50 feet, the ferrous iron concentration was relatively homogeneous, ranging from 710 to 740 mg/L.

Total iron concentrations also increased with increasing depth to a depth of approximately 50 feet (930 mg/L at 2 feet to 1,050 mg/L at 50 feet). Below 50 feet, the total iron concentration was relatively homogeneous, ranging from 1,020 to 1,050 mg/L.

1.2.2.5 Dissolved Inorganic Carbon

The DIC concentrations increased from the surface (1 mg/L DIC at 0.5 feet) to a depth of 50 feet (21 mg/L DIC). Below 50 feet, the DIC was relatively homogeneous with concentrations ranging from 19 to 25 mg/L.

1.3 Discussion

1.3.1 Physical Parameters of the Berkeley Pit Lake

It is essential to know the physical parameters of the Berkeley Pit lake because they are what control many of the processes that occur in the water column. The surface area and total volume data with respect to water level elevation are presented in Table 1-4.

The surface area of the Pit lake controls the available area for oxygen transfer and sunlight radiation into the lake. An increase in surface area increases the amount of ferrous iron that can be oxidized to ferric iron. It also increases the amount of evaporation that may occur as well as the volume of water that can be heated or cooled due to seasonal climate changes. Figure 1-1 shows the relationship between water level and surface area. During the time of sampling, the surface area was approximately 12,000,000 ft^2 (280 acres). At the critical water level (5,410 feet), the surface area will be almost double (22,000,000 ft^2 or 500 acres) what it was when this project was completed.

The volume of the Berkeley Pit lake is important for determining the amount of water that must be treated by either in situ or ex situ technologies.

The volume combined with the concentrations of

the metals within the water column will give an approximate mass of metals that must be immobilized or isolated. As of May 1998, the volume of the Berkeley Pit lake was estimated to be 3.9 billion cubic feet. At the critical water level, the estimated volume will be 9.1 billion cubic feet. Figure 1-2 shows the relationship between water level and estimated volume.

The surface area to total volume relationship is also an important relationship because it determines what fraction of the water is in contact with the atmosphere. As the Pit fills, the surface area-to-volume ratio decreases. Therefore, as the water level approaches the critical water level, the water in contact with the atmosphere will become a smaller fraction of the total volume (see Figure 1-3). This ratio is dependent on the depth of the upper layer of water that can come in contact with the surface due to mixing. However, the increased surface area will increase the amount of water that may be evaporated.

The relative depth of a pit lake has been used frequently to determine if a Pit lake will have a complete turnover of the water column, i.e., the water column will become completely mixed by seasonal turnover events or the water column will be permanently stratified by either a thermal or a chemical stratification depending on the relative depth (Ref. 3). Most natural lakes have a relative depth less than 5% that undergo seasonal turnover, whereas most pit lakes have relative depths ranging from 10% to 50%. Using the data from the 1993 Canonie report (Ref. 4), the relative depth of the Berkeley Pit lake ranges from 20% to 23%. In both cases, the relative depth would represent a lake that would not be expected to have a complete seasonal turnover.

1.3.2 Seasonal Variations of the Water Column

If it is assumed the November 1997 sample set was a typical fall profile and the May 1998 sample set was a typical spring profile, then some

seasonal trends begin to emerge. It is the upper 25 feet of water that seems to differ between the two seasons that were sampled for this study. The parameters that differ the most between the fall and spring profiles include temperature, E_H, SC, DO, inorganic carbon, and iron speciation and concentrations.

The temperature profiles for both fall and spring seem typical of a lake in this region (see Figure 1-4). Both profiles were affected to a depth of approximately 50 feet. The November profile showed cooler water above warmer water. In a natural lake, these conditions would favor a turnover event if enough wind energy was imparted on the upper layer of water. However, in the Berkeley Pit lake, the difference in SC between the surface water and the deep water may inhibit a turnover event from occurring in the Pit lake. This density difference would certainly require more wind energy to induce mixing. The May profile showed that the water was warmest near the surface and gradually decreased with increasing depth. This would be typical of a lake in spring when the lake is subjected to warmer atmospheric temperatures and more direct sunlight. These same temperature trends were also reported by Doyle et al. (Ref. 3) for the Berkeley Pit lake in 1991/92.

The E_H profiles support the idea of a chemical stratification of the Pit lake (see Figure 1-5). Although the data suggests that the E_H of the deep water changed between fall and spring, it is believed this discrepancy is caused by an inaccurate calibration of the Dataronde. This was verified by the iron speciation results, which suggest that the difference is not as great as that recorded by in situ measurements. However, trends for each data set could be used because the measurements were precise, although not accurate. The sharp decrease in E_H in the fall occurred between 25 and 50 feet. In the spring, the sharp decrease in E_H occurred between 5 and 20 feet. These profiles would suggest that the

chemical stratification location changes with the seasons. As spring progresses to fall, the zone where the E_H changes shifts to greater depths due to other controlling parameters. Between fall and spring, data suggests there is some mixing between the deeper water and the surface water resulting in a more homogeneous body of water.

The SC profiles also support the idea that chemical stratification occurs in the Pit lake (see Figure 1-6). Although the two data sets suggest the deeper water had differing specific conductivities, it is believed to be a calibration discrepancy between the two dates the samples were collected. However, the results are believed to be precise. Chemical stratification based on SC measurements was between 25 and 50 feet for the fall sample set and between 5 and 20 feet for the spring sample set. These chemical stratification depths correspond quite well with the depths predicted by the E_H measurements.

The DO profiles are different between the two seasons (see Figure 1-7). The large difference between the deep water in fall and spring is most likely because a zero DO standard and a saturated air standard were used for calibration in the spring samples whereas in the fall samples, only a saturated air standard was used. The fall DO profile showed a penetration of oxygen to a depth of 10 feet while the spring DO profile showed a depletion to a depth of 25 feet. This data suggests that the DO in the surface water was consumed in the spring by the oxidation of ferrous iron to ferric iron. In the fall, the majority of the iron in the surface water had already been oxidized to ferric iron, allowing a deeper penetration of DO before it was consumed.

Fall and spring profiles show different trends in the DIC (see Figure 1-8). Both show a similar and relatively homogeneous concentration of DIC below a depth of 50 feet. Above 50 feet, however, the profiles were noticeably different. In the spring profile, the DIC profile showed a

constant decrease toward the surface whereas in the fall profile, the DIC concentration was homogeneous to a depth of 25 feet. These profiles are similar to the profiles for ferrous iron concentrations.

It is the iron speciation and concentrations that have the greatest relevance to the sedimentation rate determination; consequently, they will be discussed in detail below.

1.3.2.1 Fall Profile

The average fall iron speciation profile shows that there was a dramatic change in the water column between 25 and 50 feet (see Figure 1-9). This is also supported by the shift in the E_H and the SC over the same depths. The surface water was dominated by ferric iron (86%) while the deep water was dominated by ferrous iron (77%). This zone between the two different waters has been termed the chemocline. The chemocline is similar to a thermocline, but instead of a rapid change in temperature with depth, the chemocline has been defined as a rapid change in salinity with increasing depth (Ref. 2). In the case of the Berkeley Pit Lake, the chemocline is referred to as the zone where the major valence of iron changes from (III) to (II).

The average fall iron speciation profile also shows that the total iron concentration decreased from 1,000 mg/L iron at 50 feet to 850 mg/L near the surface. Below the chemocline, the ferrous iron and total iron concentrations were somewhat constant at 800 and 1,000 mg/L, respectively. It is also interesting to note that not all of the iron in the surface water is completely oxidized. The ferrous iron concentration is relatively constant from 25 feet to the surface (120 mg/L). This may support the reasoning behind the decrease in DO concentrations with increasing depth for the fall profile.

1.3.2.2 Spring Profile

The spring iron speciation profile collected in May 1998 had a similar appearance to the fall profile (see Figure 1-10). The major difference being that the chemocline was between 8 and 20 feet instead of 25 and 50 feet. This chemocline location is again supported by the E_H and SC profiles. The ferric iron accounted for 73% of the iron on average in the epilimnion (surface water). In the hypolimnion (deep water), the ferrous iron was approximately 70% of the iron. The total iron concentration decreased from a depth of 20 feet (1,000 mg/L) to the surface (925 mg/L).

1.3.2.3 Comparison of the Fall and Spring Profiles

When the fall and spring iron speciation profiles are overlaid, a few possible trends begin to emerge. These trends include a shift in the chemocline to a greater depth and a depletion of iron in the surface water as spring progresses to fall.

1.3.2.4 Shift in the Chemocline

There are many factors that could be influencing the vertical position of the chemocline. Some of these factors include temperature, wind, DO penetration, light penetration, and surface runoff and precipitation.

1.3.2.4.1 Temperature

Temperature could control the depth of the chemocline by stratifying the Pit Lake based on density. During the summer months, the surface water is warmer than the deeper water. This stratification keeps the surface water from mixing with the deeper water less than if there were no thermocline. The difference in SC between the surface water and the deep water would create an even larger difference in density. An increase in temperature may also have a significant influence on the rate of precipitate formation. This suggestion depends on the extent of supersaturation in the water with respect to the precipitates formed and the sensitivity of the kinetic rate to temperature changes. To be more specific, the equilibrium constant is dependent on

temperature through the enthalpy of formation and the heat capacity of the precipitate formed (Ref. 5).

1.3.2.4.2 Dissolved Oxygen Penetration
Dissolved oxygen could control the chemocline depth by oxidizing the ferrous iron to ferric iron. As spring progresses to fall, ferrous iron near the surface is oxidized, allowing DO to penetrate deeper into the body of water. This control is highly dependent on the temperature of the water because the solubility decreases with an increase in temperature (Ref. 6).

1.3.2.4.3 Wind
Wind could be controlling the chemocline depth by mixing the water near the surface. When the surface water is mixed, it distributes DO more evenly throughout the upper section of the Pit Lake when compared to a stagnant environment. This wind-induced mixing may also redistribute the warm surface water to greater depths. Stevens and Lawrence (Ref. 7) showed the importance of gathering wind amplitudes at the Pit lake surface and the effects wind could have on mixing for a pit lake in British Columbia. This parameter is difficult and costly to obtain; therefore, it was not measured for this project.

1.3.2.4.4 Light Penetration
Light penetration into the upper foot of water may be acting as a photocatalyst for the oxidation/precipitation reaction. As the sun progresses towards the summer equinox, the UV radiation reaching the Pit Lake increases. The UV radiation can cause the iron(II)/iron(III) sulfate colloidal complexes to create oxygen and/or hydrogen peroxide, thus increasing the oxidation rate well beyond what would be predicted for an abiotic reaction (Ref. 8). This increased rate could allow the chemocline to drop further than would be expected relative to the temperature and DO concentrations in the water column.

1.3.2.4.5 Surface Runoff and Penetration
Surface runoff and rainfall over the summer months could dilute the surface water and create an appearance that the chemocline had dropped. This was one of the conclusions drawn by the study of the Berkeley Pit in 1987 (Ref. 1). However, this study was conducted before the surface water runoff (Horseshoe Bend) was diverted from entering the Pit Lake. Since the precipitation in the Butte area is roughly equivalent to the evaporation, it would be reasonable to say that this parameter has no net effect on the position of the chemocline (Ref. 9).

When all of these parameters are compared, it becomes evident that the control of the chemocline depth is a complex situation. There are parameters mentioned above and others that were not considered in this report (bacterial reduction of ferric iron, photosynthesis by algae, and other biological activities) that all play a role in the depth of the chemocline. Sloughing of wall rock to the bottom of the Pit Lake can have a major effect on the distribution of precipitates throughout the lake.

1.3.2.5 Depletion of Total Iron in the Surface Water
When the two profiles are compared, it can be seen that the total iron concentration was lower in the shallow waters, i.e., the water above the chemocline, than in the deeper water for both seasons (see Figure 1-11). It seems that after the iron was oxidized, it was removed from the surface water.

To verify this was not an artifact of the analysis method employed, the results from the 1,10-phenanthroline analysis method were compared to the results from the ICP-AES. The difference between the two analytical methods was within 10% relative error for all of the samples analyzed. There was some systematic error associated with one of the two methods employed. This bias was recognized by the ratio of the ICP to 1,10-phenanthroline consistently being greater than 1,

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i.e., there was not a single instance were the 1,10-phenanthroline result was higher than the result from the ICP.

Regarding the question of what could be causing the depletion of total iron in the shallow water, this is a complex issue, much like the control of the chemocline depth, and some of the same parameters will be in control here as well. These include precipitation of iron followed by gravity settling and dilution of the surface water due to surface runoff. Precipitation and settling of the iron precipitates formed probably has the largest impact on the total iron concentration. Since the diversion of the Horseshoe Bend water, there is no dilution of the surface water on an annual cycle because there is no net precipitation for the Butte area. The only time of year when dilution is a significant factor is early spring when the ice and snow deposited on the Pit lake surface melts. Dilution can also be ruled out because a majority of the elements present in the Pit lake water are relatively homogeneous with respect to depth. In fact, the fall metals depth profiles show a slight increase in concentrations in the surface water when compared to the deep water. This data might suggest that evaporation does play a minimal role in the concentrations of the majority of the metals.

It would be reasonable to think that the precipitates formed are removed from the surface water and added to the deep water. One would suspect that the fate of this iron could be to either settle to the bottom or dissolve at depth.

For the precipitates to settle to the bottom and accumulate, the equilibrium must favor the formation of the precipitates under the reduced environment and colder temperatures found in the deeper water, otherwise the iron precipitates will dissolve and increase the ferric iron concentration at depth. The equilibrium constant for dissolution is dependent on the particle size of the precipitates. As the particle size increases, the precipitates become more thermodynamically stable (Ref. 10). If the iron precipitates formed at the surface are unstable at depth, it is possible that the precipitates dissolve and reprecipitate as more stable precipitates that will reach the bottom.

It is possible for the iron precipitates to dissolve and increase the ferrous iron concentration below the chemocline due to the activity of iron-reducing bacteria. However, many of these bacteria, e.g., *Geobacter metallireducens*, *G. sulfurreducens*, and other sulfur-reducing strains, require anaerobic conditions, i.e., $E_H < 0$ mV, and/or an absence of sulfate (Ref. 11), neither of which has been found in the water column in the Berkeley Pit Lake. The other problem with this suggestion is that there is no support for the bacteria that may be present in the water column. Unlike a subsurface or wetland environment where there are many sites for the bacteria to adhere, there are only floating timbers at the surface and the precipitates, which does not allow for the bacteria to reduce the iron at a significant rate.

From these profiles, it cannot be determined whether the iron precipitates formed near the surface reach the bottom or are dissolved at depth. The problem stems from the fact that there is no appreciable increase in the total iron concentrations below the chemocline. If the iron were dissolving below the chemocline, one would expect to find an increase of total iron in this region. The same reasoning applies to the case of the precipitates settling to the bottom. The problems with this reasoning are that not all of the iron is precipitated at the same time during the year and the precipitates formed are colloidal, producing a wide range of particle sizes. These two factors allow the iron precipitates formed to be distributed over a greater depth than what might be expected. Therefore, a sharp increase in total iron may not be seen for either of these proposed ideas.

1.3.3 Comparison of the Water Chemistry

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The data collected by Davis and Ashenberg in 1987 (Ref. 1) was compared to the data collected in November 1997 for this project. From this comparison, it was determined that the water chemistry had changed dramatically with respect to some of the major ions present in solution. Table 1-5 shows a comparison of the average shallow waters and the average deep waters for both sample sets.

It can be seen from Table 1-5 that some of the major ions present have increased in concentration over the last 10 years. The most noticeable changes occurred for magnesium, aluminum, manganese, and zinc. These increases may be a sign that these elements have not reached concentrations great enough to allow for control by precipitation. However, this does not mean that all the remaining elements that have not changed are under control due to a solid phase precipitating, it may be the case that the inflowing water chemistry has changed over the past 10 years.

Another major change between the data from 1987 and the data from 1997 was the speciation of the iron. Figure 1-12 shows the iron speciation for 1987. In 1987, the ferric iron concentrations in the deep water were reported to be approximately 1% (10 mg/L) of the total iron (Ref. 1). By 1997, the ferric iron concentrations in the deep water had increased to be approximately 23% (230 mg/L) of the total iron. This significant increase in ferric iron at depth could possibly be an indication that the entire water body is becoming more of an oxidized environment as the Pit fills. An aspect that must be considered is the speciation and concentration of the iron entering the lake system, i.e., to know the ability of the inflow water to buffer the E_H.

1.3.4 Speciation of Precipitates

Two different types of precipitates were found in the SEM/EDX study of the precipitates collected from the Berkeley Pit lake water. These precipitates included one that was filamentous and dominated by sulfur and calcium and the other that was globular and dominated by sulfur and iron.

The filamentous precipitate had a calcium-to-sulfur ratio close to 1:1. The oxygen-to-sulfur ratio was close to 6:1. From these two ratios, it could easily be determined that the filamentous precipitates were gypsum ($CaSO_4 \cdot 2H_2O$). Additional iron and silicon associated with the gypsum was more than likely adsorbed to the surface of the gypsum crystals or salted out on the surface when the sample was dried. The gypsum crystals accounted for approximately 1% to 2% of the total precipitates collected. The majority of the precipitates were the globular precipitates.

The globular precipitates had an iron-to-sulfur ratio close to 8:1. The remainder of the elements, excluding oxygen, were found only in trace amounts. Possible iron precipitates that may be forming in the Berkeley Pit Lake include jarosite, $(H,K,Na)Fe_3(OH)_6(SO_4)_2$; schwertmannite, $Fe_8O_8(OH)_6SO_4$; and goethite, a-$FeOOH$ (Ref. 12). The iron-to-sulfur ratio would suggest that the globular precipitate was either hydronium jarosite or schwertmannite. However, the morphology of the iron precipitates would support only schwertmannite because the morphology of jarosite is pseudocubic and goethite is angular (Ref. 13). The formula given above for schwertmannite is the ideal formula; however, the amount of sulfate incorporated into the precipitate structure can change the formula to $Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$. Thus, the iron-to-sulfur ratio would be closer to 4:1 than 8:1. Therefore, it is believed that the globular precipitates were schwertmannite with additional sulfate adsorbed to the surface of the precipitate.

Although no jarosite was found during the SEM/EDX study, this does not mean that jarosite was not precipitating in the surface water. The

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potassium concentration profile was one of the few elements that showed a decrease near the surface when compared to the deeper water. This profile suggests there was some potassium-jarosite (K-jarosite) precipitating near the surface (see Figure 1-13).

The reduction in arsenic concentrations near the surface may also be due to the formation of iron precipitates (see Figure 1-14). One the few solid phases that may control the arsenic concentration in the Pit lake water is scorodite ($FeAsO_4 \cdot 2H_2O$); however, scorodite controls the arsenic concentration only between pH 4 and 5 under this type of environment (Ref. 1). A more likely control of the arsenic is through adsorption mechanisms to the iron precipitates. Most iron precipitates have isoelectric points between pH 5 to 9, thus the surface charge on iron precipitates in the Berkeley Pit lake water would be highly positive (Ref. 14).

1.3.5 *Predicted Sedimentation Rate*
The sedimentation rate is largely dependent on the types of precipitates forming and the settling characteristics of the precipitates. Settling characteristics tend to be dependent on the type of precipitate as well as the presence of other precipitates, which might act as a seed for the formation of larger agglomerations, e.g., gypsum for schwertmannite. Since the equilibrium constants for many of the iron precipitates can change by two orders of magnitude, between 4 °C and 30 °C, it would be reasonable to expect the sedimentation rate to change from spring to summer to fall. Many of the iron precipitates have a retrograde solubility, i.e., less soluble at higher temperatures; therefore, the sedimentation rate would be expected to be greatest over the summer months when the water temperature of the surface water is greatest (Ref. 14). However, landslide events can drastically change the sedimentation rate over a short period of time.

The November 1997 data set was used to determine the sedimentation rate for 1997, prior to the landslide event on September 29, 1998. For this determination, it was assumed that no more metal precipitation occurs in the year after this November sample set, and all of the potassium removed from the surface water was in the form of K-jarosite. It was also assumed that the remainder of the iron removed from the surface water was precipitated as schwertmannite (with the greatest amount of sulfate incorporated into its structure, $Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$). The amount of gypsum settling was assumed to be less than 1% of the total amount of iron settling; therefore, it was considered negligible and unnecessary to complete this rough estimation.

The amount of iron removed in 1997 from the surface water layer varied between 100 and 250 grams/cubic meter (g/m^3) [0.1-0.24 ounces per cubic feet (oz/ft^3)]. The amount of potassium removed varied between 1 and 2 g/m^3 (0.001-0.002 oz/ft^3). When the depth of the chemocline and the surface area of the Pit Lake in November 1997 are included, the total amount of iron removed varied between 1,200 to 3,600 tons per year, and the total amount of potassium removed varied between 15 to 30 tons per year. Therefore, approximately 1% to 5% of the iron was removed as K-jarosite (200 to 400 tons K-jarosite per year), and the remainder was removed as schwertmannite (2,300 to 6,200 tons per year).

It should be emphasized that this is just a rough estimate of the amount of precipitates removed from the surface water over a yearly cycle, and the percentage of these precipitates that reaches the bottom of the Pit Lake is unknown.

1.4 Conclusion
From this project, it was determined that the water chemistry of the Berkeley Pit Lake varies with the extent of filling and with the changes in the seasons. The amount of precipitates removed from the surface water layer depends on the surface area and climatic changes associated with

the four seasons. The Berkeley Pit lake can be divided into two different zones: the surface water and the deep water. The water chemistry and depth of the surface water is dependent on the season, whereas the deep water chemistry is relatively constant throughout the yearly cycle.

The precipitates that were found using an SEM/EDX in the Berkeley Pit lake water included gypsum and schwertmannite. From the depth profile results for the fall sample set, it was concluded that some K-jarosite was also removed from the surface water. The reduction in arsenic in the surface water was more likely due to adsorption and not direct precipitation.

A rough estimation of the sedimentation rate was determined. Approximately 100 to 250 grams of iron per cubic meter were removed from the surface water per year. For 1997, this was approximately 1,200 to 3,600 tons of iron per year. In the major precipitate forms, this equates to 200 to 400 tons of K-jarosite and 2,300 to 6,200 tons of schwertmannite per year. This rough estimation assumes that all of the iron removed from the surface water reached the bottom of the Pit Lake and did not redissolve.
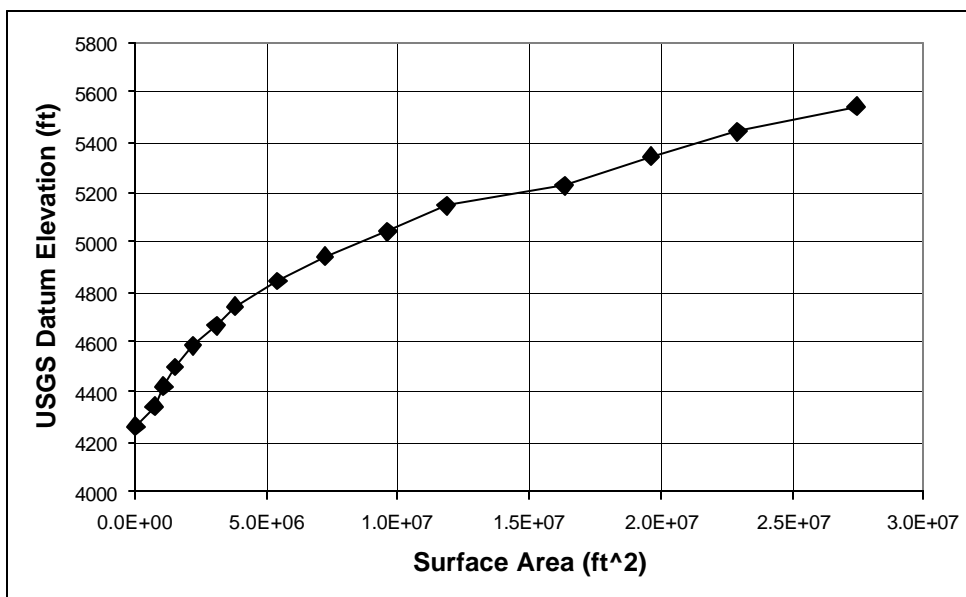
Figure 1-1. Relationship between the Berkeley Pit lake water level and the surface area.

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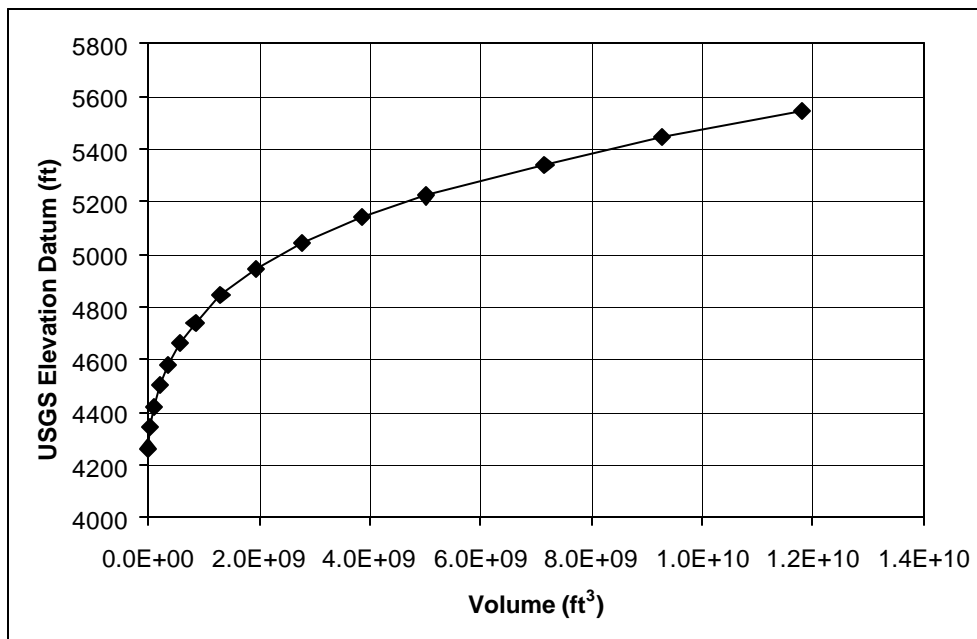
Figure 1-2. Berkeley Pit water level versus total volume.
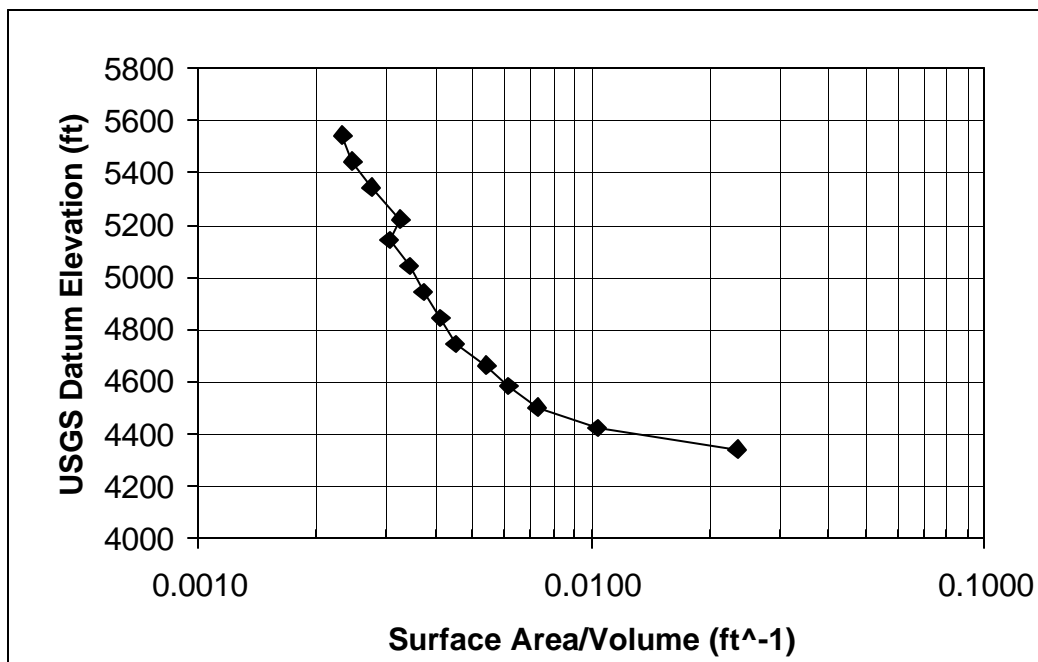
Figure 1-3. Berkeley Pit lake water level versus surface area/volume ratio.
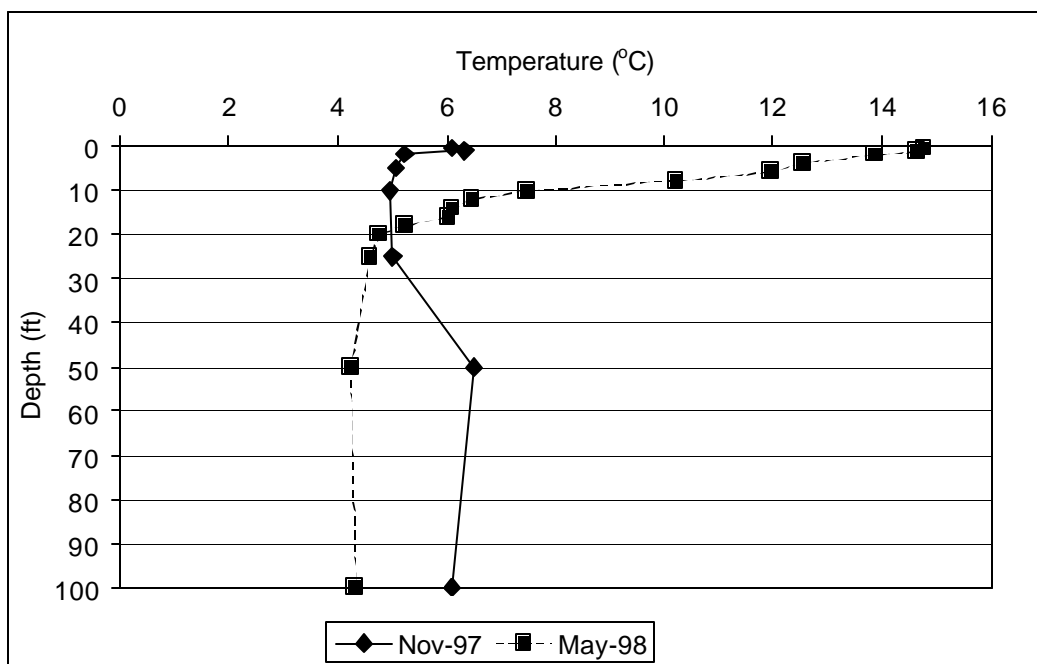
Figure 1-4. Temperature profiles of the upper 100 feet of the Berkeley Pit lake.

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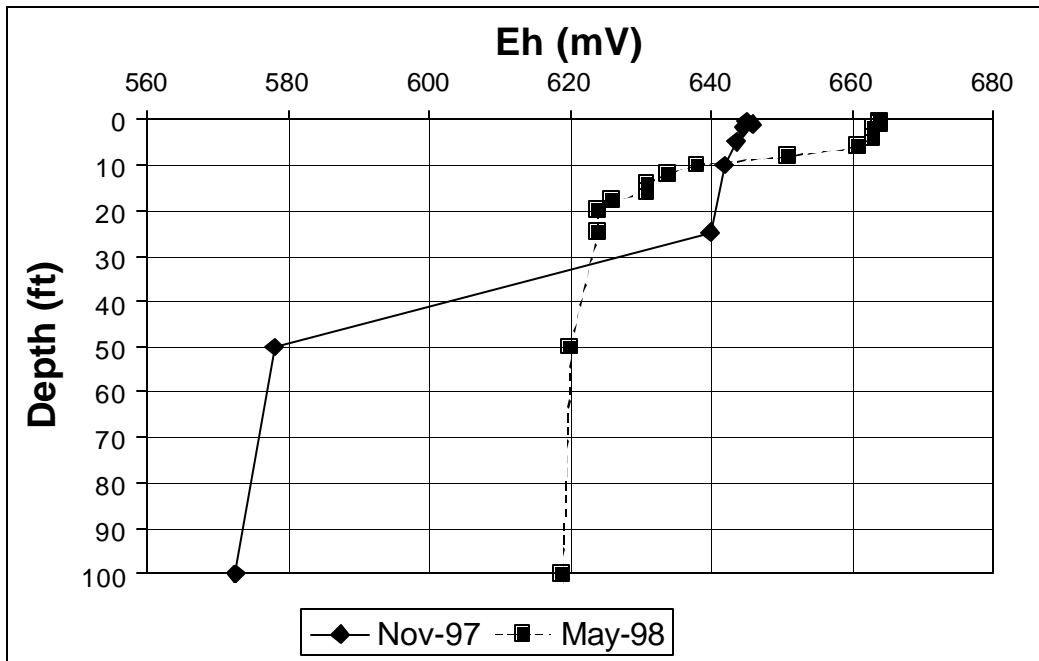
Figure 1-5. E$_H$ profiles of the upper 100 feet of the Berkeley Pit lake.
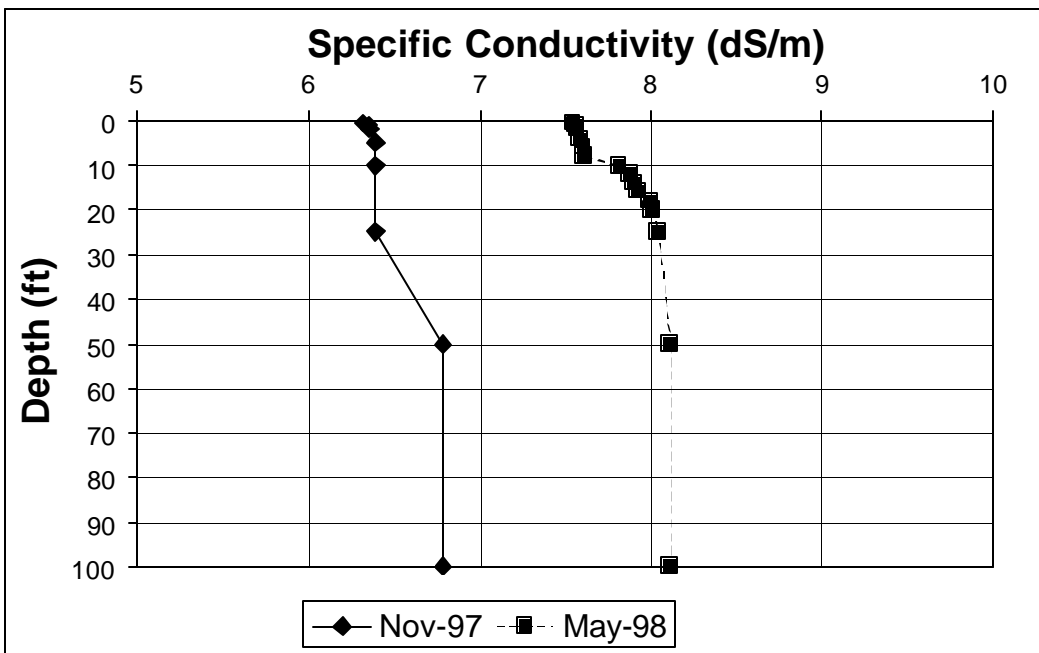
Figure 1-6. Specific conductivity profiles of the upper 100 feet of the Berkeley Pit lake.
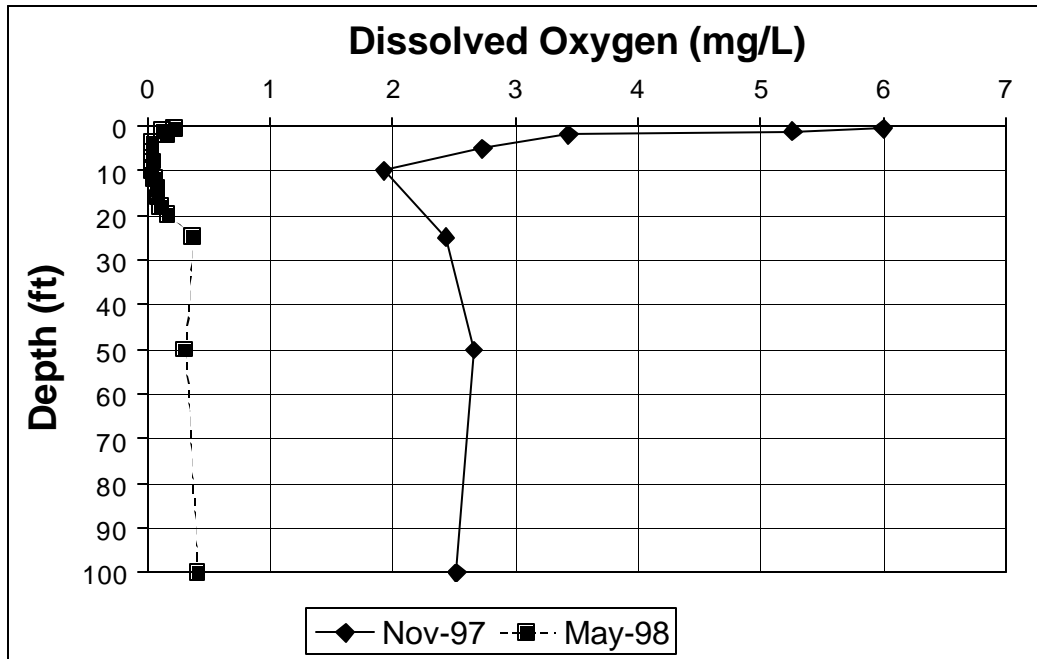
Figure 1-7. DO profiles of the upper 100 feet of the Berkeley Pit lake.
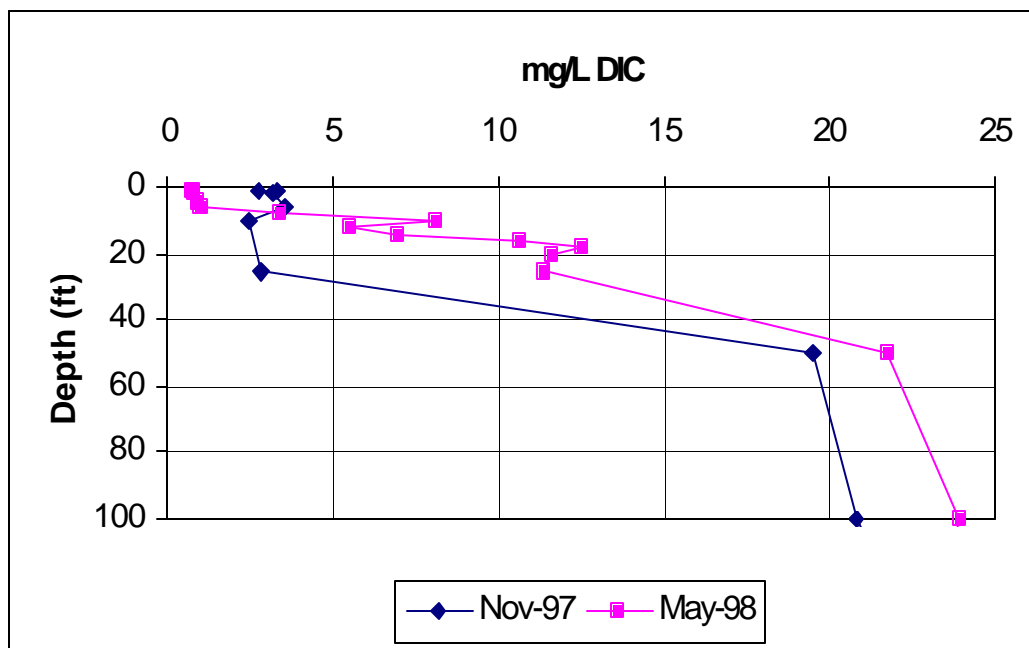
Figure 1-8. DIC profiles of the upper 100 feet of the Berkeley Pit lake.
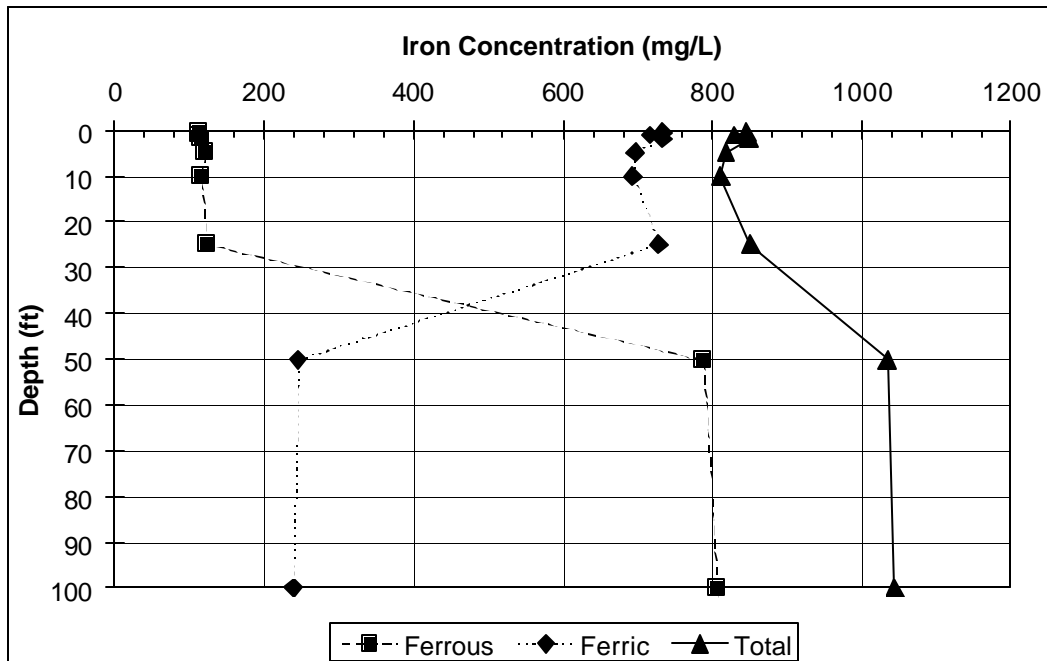
Figure 1-9. Fall 1997 average iron speciation profile of the upper 100 feet of the Berkeley Pit lake.
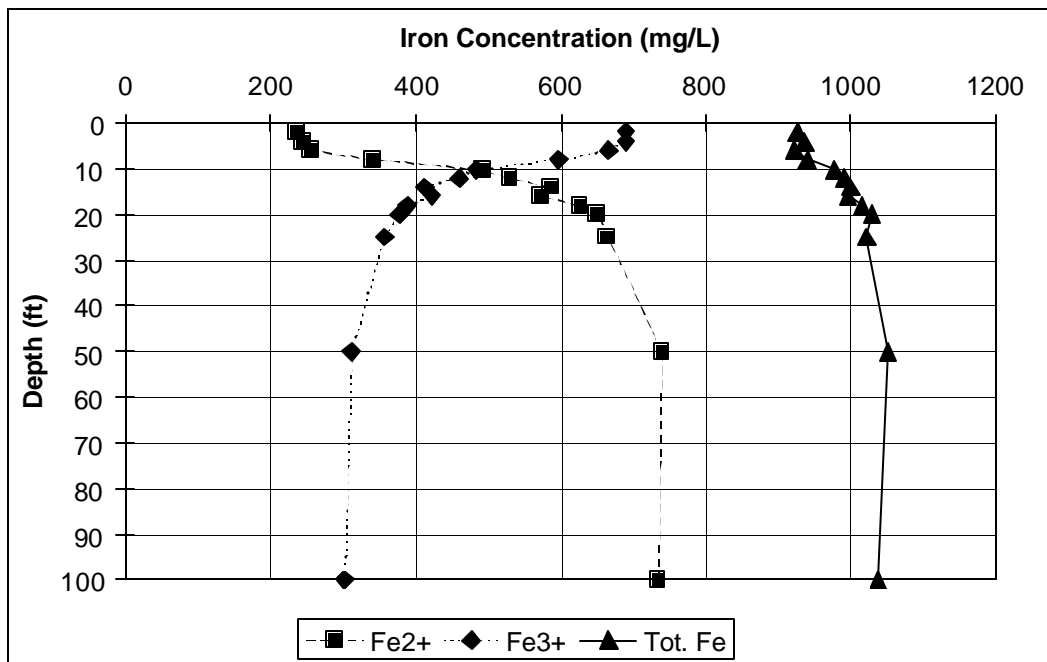
Figure 1-10. Spring 1998 iron speciation profile of the upper 100 feet of the Berkeley Pit lake.
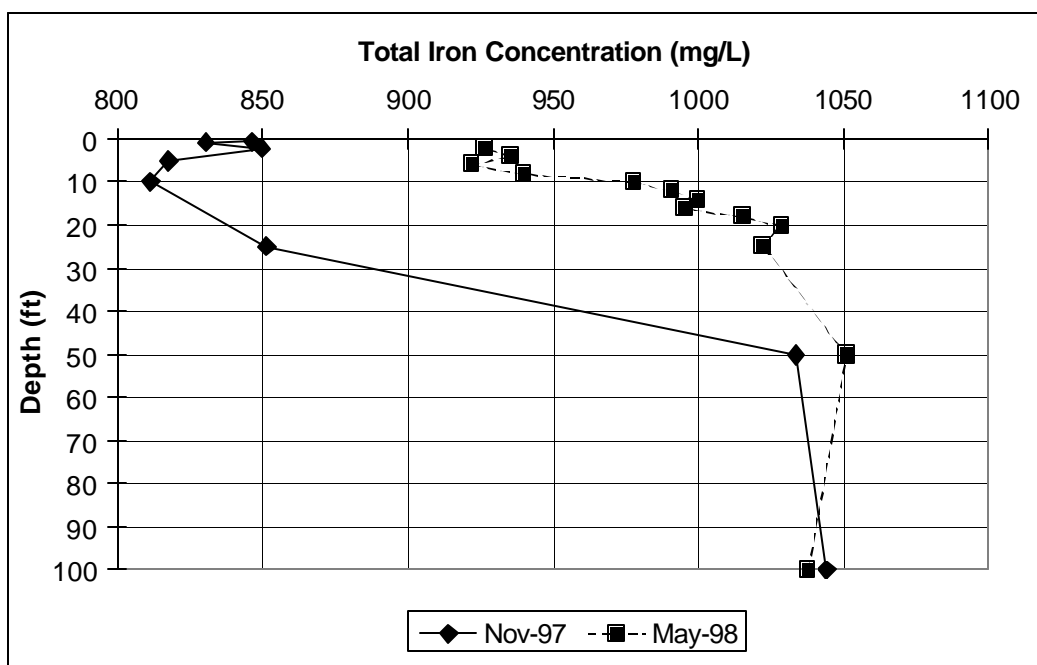
Figure 1-11. Comparison of the total iron concentrations for spring and fall in the upper 100 feet of the Berkeley Pit lake.
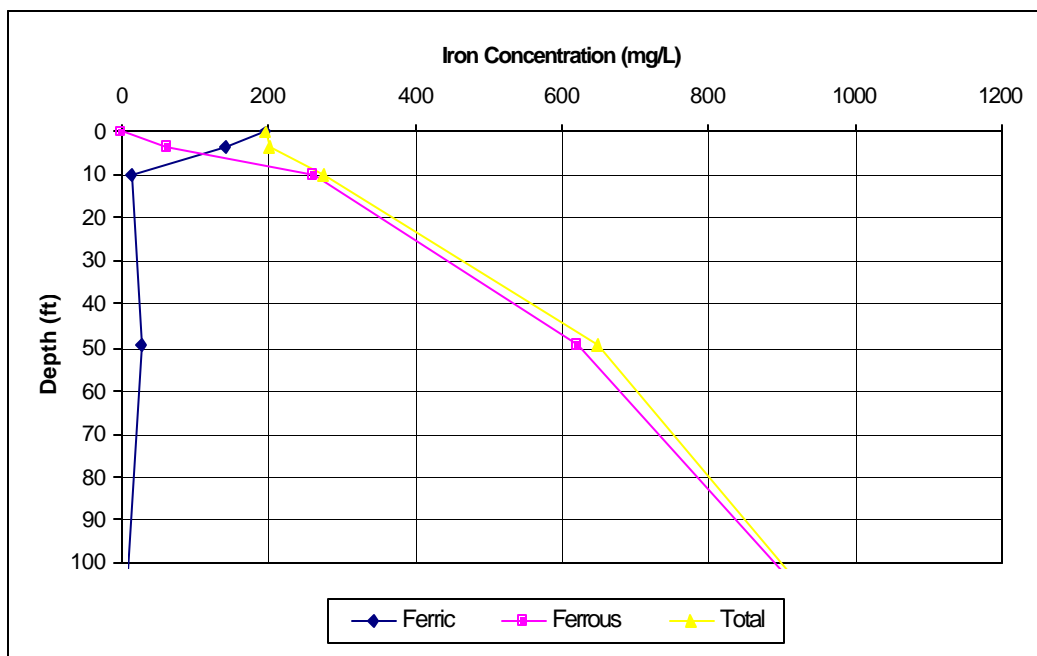
Figure 1-12. 1987 iron speciation profile of the upper 100 feet of the Berkeley Pit lake (Ref. 2).

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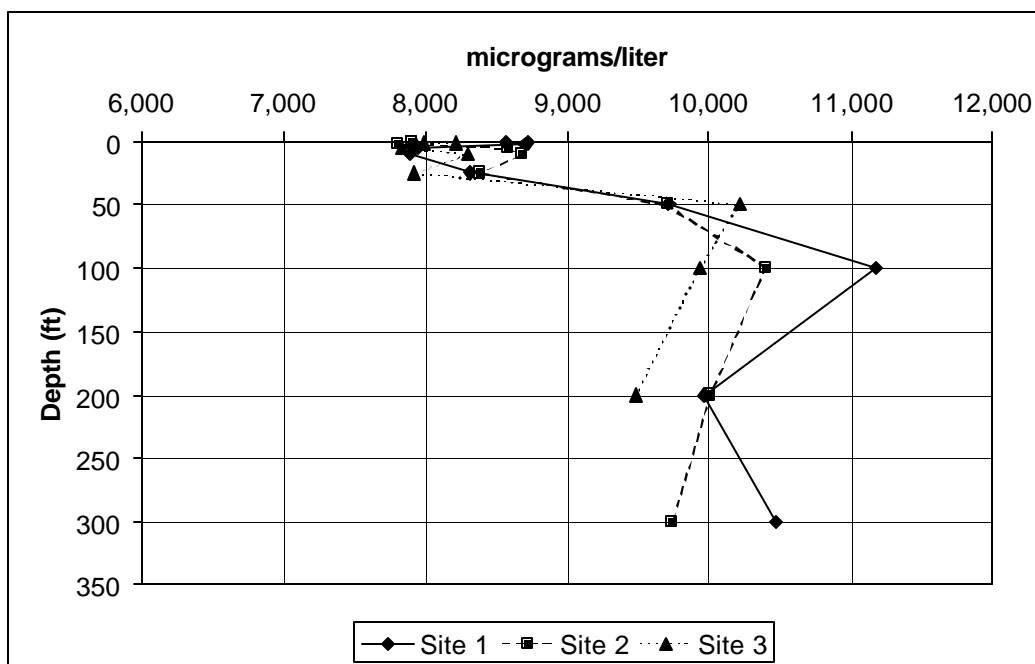
Figure 1-13. November 1997 dissolved potassium concentration profile of the Berkeley Pit lake.
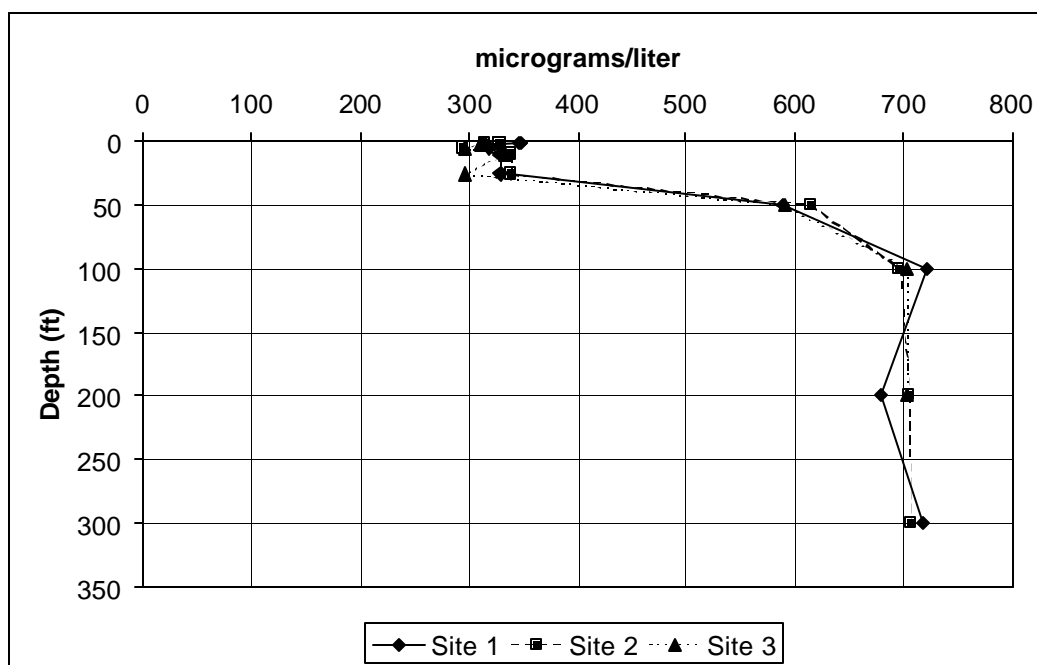
Figure 1-14. November 1997 dissolved arsenic concentration profile of the Berkeley Pit lake.

Table 1-1. November 1997 Total Recoverable Metals

Element	Method Detection Limit	Average	Minimum	Maximum	RSD (%) (n=28)
Aluminum (Al)	120	305,900	294,700	322,600	1.9
Arsenic (As)	20	460	310	760	38.5
Boron (B)	100	4,500	4,100	5,200	10.0
Cadmium (Cd)	10	2,330	2,120	2,530	4.0
Calcium (Ca)	40	480,240	466,090	489,600	1.3
Cobalt (Co)	10	1,770	1,630	1,900	3.3
Copper (Cu)	20	211,750	203,830	217,720	1.9
Iron (Fe)	20	998,620	910,250	1,165,900	9.5
Magnesium (Mg)	70	524,700	497,500	542,900	2.8
Manganese (Mn)	20	245,000	231,000	255,200	3.3
Nickel (Ni)	20	1365	1249	1475	4.2
Phosphorous (P)	60	670	550	850	11.4
Potassium (K)	150	8,900	7,600	10,300	9.4
Silicon (Si)	80	55,100	53,800	55,900	1.1
Sodium (Na)	1,100	120,000	115,000	128,000	2.6
Strontium (Sr)	50	1,300	1,200	1,500	4.1
Sulfur (S)	100	2,750,700	2,673,600	2,791,600	1.1
Zinc (Zn)	10	657,290	636,680	675,460	1.6

*The samples used for creating this table were: Location 1—0.5, 1, 2, 5, 10, 25, 50, 100, 200, 300 feet; Location 2—0.5, 1, 2, 5, 10, 25, 50, 100, 200, 300 feet; and Location 3—0.5, 1, 2, 5, 10, 25, 50, 100, 200 feet.

*All concentrations are in Fg/L.

Table 1-2. November 1997 Total Dissolved Metals

Element	Method Detection Limit	Average	Minimum	Maximum	RSD (%) (n=29)
Aluminum (Al)	120	299,400	291,100	309,600	1.4
Arsenic (As)	20	460	300	720	39.0
Boron (B)	100	4,200	3,800	4,800	10.0
Cadmium (Cd)	10	2,320	2,170	2,460	3.3
Calcium (Ca)	40	465,000	452,960	486,710	1.5
Cobalt (Co)	10	1,720	1,630	1,810	2.8
Copper (Cu)	20	209,420	203,070	216,980	1.6
Iron (Fe)	20	950,450	849,090	1,082,970	10.3
Magnesium (Mg)	70	515,700	495,300	539,000	2.5
Manganese (Mn)	20	236,700	225,070	252,200	3.1
Nickel (Ni)	20	1,300	1,220	1,380	3.3
Phosphorous (P)	60	630	530	770	12.1
Potassium (K)	150	8,900	7,800	11,200	11.2
Silicon (Si)	80	54,500	54,000	55,700	0.9
Sodium (Na)	1,100	116,000	111,000	124,000	2.4
Strontium (Sr)	50	1,370	1,280	1,490	4.1
Sulfur (S)	100	2,746,000	2,713,900	2,810,900	0.9
Zinc (Zn)	10	636,200	617,690	663,660	1.5

*The samples used for creating this table were: Location 1—0.5, 1, 2, 5, 10, 25, 50, 100, 200, 300 feet; Location 2—0.5, 1, 2, 5, 10, 25, 50, 100, 200, 300 feet; and Location 3—0.5, 1, 2, 5, 10, 25, 50, 100, 200 feet.

*All concentrations are in Fg/L.

Table 1-3. May 1998 Total Dissolved Metals

Element	Method Detection Limit	Average	Minimum	Maximum	RSD (%) (n=27)
Aluminum (Al)	120	297,733	291,159	305,368	1.4
Arsenic (As)	20	627	367	823	25.0
Boron (B)	100	2,400	2,100	2,600	5.5
Cadmium (Cd)	10	2,216	2,073	2,374	3.4
Calcium (Ca)	40	468,124	459,073	478,894	1.1
Cobalt (Co)	10	1,680	1,570	1,770	3.2
Copper (Cu)	20	198,138	195,819	202,827	0.9
Iron (Fe)	20	1,061,375	954,955	1,135,899	5.2
Magnesium (Mg)	70	502,415	489,772	516,993	1.4
Manganese (Mn)	20	234,354	230,669	240,284	0.9
Nickel (Ni)	20	1,261	1,184	1,335	3.2
Phosphorous (P)	60	770	620	920	9.8
Potassium (K)	150	8,254	6,946	9,401	8.2
Silicon (Si)	80	54,049	52,823	55,215	1.2
Sodium (Na)	1,100	102,878	95,841	108,963	3.1
Strontium (Sr)	50	1,250	1,120	1,510	8.0
Sulfur (S)	100	2,860,897	2,782,059	2,949,589	1.4
Zinc (Zn)	10	645,076	631,113	666,172	1.0

*The samples used for creating this table were: 0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 2 at 50, 2 at 100, 200, 300, 400, 500, 600, 700, 800, 880, and 888 feet.

*All concentrations are in Fg/L.

Table 1-4. Berkeley Pit Surface Area and Volume Calculations

USGS Datum (ft)	Depth (ft)	Contour Area (ft²)	Volume between Contours (ft³)	Summation of Volume (ft³)
4,263	0	4.650 E+4	---	---
4,343	80	7.533 E+5	3.199 E+7	3.199 E+7
4,423	160	1.099 E+6	7.410 E+7	1.061 E+8
4,503	240	1.537 E+6	1.055 E+8	2.115 E+8
4,583	320	2.226 E+6	1.505 E+8	3.621 E+8
4,663	400	3.101 E+6	2.131 E+8	5.751 E+8
4,743	480	3.829 E+6	2.772 E+8	8.523 E+8
4,843	580	5.432 E+6	4.631 E+8	1.315 E+9
4,943	680	7.259 E+6	6.346 E+8	1.950 E+9
5,043	780	9.629 E+6	8.444 E+8	2.794 E+9
5,143	880	1.188 E+7	1.075 E+9	3.870 E+9
5,223	960	1.632 E+7	1.128 E+9	4.997 E+9
5,343	1,080	1.961 E+7	2.156 E+9	7.153 E+9
5,443	1,180	2.291 E+7	2.126 E+9	9.279 E+9
5,543	1,280	2.744 E+7	2.517 E+9	1.180 E+10
4,852	589	5.44E+6	1.30E+9	1987
5,150	887	1.20E+7	3.90E+9	Nov-97
5,156	893	1.20E+7	3.90E+9	May-98
5,410	1147	2.20E+7	9.10E+9	Critical Level

*All of the data given above came directly from Ref. 4.

*The data presented in this second section came from *The Pitwatch*, 1998.

Table 1-5. Comparison of 1987 to 1997 Water Chemistry

	Shallow Water			Deep Water	
Analyte (mg/L	1987 (3m)	1997 (avg. 3.5m)	Analyte (mg/L	1987 (100m)	1997 (avg. 50m)
Calcium (Ca)	462	484	Calcium (Ca)	506	475
Magnesium (Mg)	201	535	Magnesium (Mg)	272	507
Sodium (Na)	72	121	Sodium (Na)	73	119
Potassium (K)	10	8	Potassium (K)	25	10
Chloride (Cl⁻)	9	20	Chloride (Cl⁻)	20	19
Sulfate (SO_4^{2-})	5,740	8,320	Sulfate (SO_4^{2-})	7060	8,180
Arsenic (As)	0.05	0.30	Arsenic (As)	0.70	0.70
Aluminum (Al)	152	310	Aluminum (Al)	206	300
Cadmium (Cd)	1.3	2.4	Cadmium (Cd)	1.9	2.2
Copper (Cu)	156	215	Copper (Cu)	218	207
Iron (Fe)	386	932	Iron (Fe)	1,040	1,123
Manganese (Mn)	95	251	Manganese (Mn)	162	235
Zinc (Zn)	280	664	Zinc (Zn)	496	646
pH	2.80	2.61	pH	3.08	2.48

*All 1987 data was duplicated from Ref. 1.

2.   Determination of Total Organic Carbon in the Berkeley Pit Lake Water

2.1   Background

Prior to this work, only one known analysis of deep water (200 feet below the surface) was done to determine organic carbon content in the Berkeley Pit lake water.   Chatham measured 5 parts per million (ppm) total organic carbon in the water (milligrams of carbon per liter of water, mg C/L). [1] Algae, bacteria, fungi, and protozoa were noted in the surface water of the Pit lake by Mitman.[2] Organic carbon would be expected from decaying algae, bacteria, fungi, and protozoa like those found in the near-surface waters on the perimeter of the Pit lake. However, many of the organisms identified are heterotrophic and require organic carbon for growth. The food requirement of these organisms indicates a separate source of organic carbon.

Organic compounds in the Berkeley Pit lake water could be the result of fuel spills or leaking from fuel or lubrication storage containers (gasoline, diesel fuel, lubricating fluids, etc.) from the days of active mining. A significant amount of machinery was abandoned in the mines prior to their flooding.[3] It is not known if all of the underground fuel and lubricating storage containers (or the contents) for this machinery were removed. Therefore, it is possible that some fraction of the organic carbon in the Pit lake water is from fuel and lubrication materials.

Runoff water and groundwater from the

surrounding watershed is also a potential source of organic carbon for the Pit lake. The Yankee Doodle watershed north of the Berkeley Pit is well covered with deciduous and coniferous trees and assorted undergrowth. The mountains surrounding Butte (the Summit Valley) are also well forested and contain a variety of undergrowth. Decomposition of these plant materials produces a heterogeneous mixture of organic compounds collectively known as humic substances. A substantial fraction of the humic material is soluble in water (Refs. 15 and 16). Drainage from the mountains recharges the groundwater in the valley. The groundwater from the area is still infiltrating the Pit; however, the surface flow from the Yankee Doodle drainage was diverted in 1997 and no longer flows directly into the Berkeley Pit.

The effects of organic carbon on the Berkeley Pit lake chemistry or any remediation of Pit lake waters depend on the types and amounts of the carbon. To understand the effects, the types and amounts of the organic carbon must be determined.

2.1.1   Heterotrophic Organisms

Many of the Berkeley Pit lake organisms, such as most of the bacteria and all protozoans, are heterotrophic. Heterotrophic organisms require organic carbon as a nutrient. Deep bodies of water recently formed from groundwater seeps often contain low amounts of organic carbon. The low carbon concentration and a lack of other nutrients can limit population sizes of heterotrophic organisms. Consequently, the carbon content in the water may adversely affect natural remediation of the Pit by the biological component of the Pit lake ecosystem.

2.1.2   Fuels and Lubricants

Hydrocarbon fuels and some lubricants contain a

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[1]William Chatham, Chemistry and Geochemistry Dept., Montana Tech of the University of Montana, personal communication, 1996.

[2]Grant Mitman, Biology Dept., Montana Tech of the University of Montana, personal communication, 1996.

[3]David Piper and Irving DeVoe, Metanetix Corp., personal communication, 1994.

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significant amount of aromatic compounds that are known to be carcinogenic and mutagenic (Ref. 17). As a result, these materials are classified as hazardous waste, and any remediation process must remove these substances from the Pit lake water. Therefore, it is necessary to know the type and amount of these compounds that are present to determine what, if any, remediation is necessary for the organic carbon.

Aromatic hydrocarbons are strong absorbers of UV radiation, and as a consequence, could serve as energy reservoirs for other photocatalyzed reactions. Aromatic molecules can also adsorb strongly to solid surfaces, which could affect precipitation reactions in the Pit lake water or during remediation work. In addition, aromatic molecules are chemically reactive (oxidation and reduction and substitution reactions being dominant). As a consequence, these compounds, if present, could be actively involved in the Pit lake chemistry or interfere with any remediation chemistry.

2.1.3 Humic Substances

Humic substances are derived from the decay of plant and animal matter by chemical and microbiological mechanisms. Formation of the humic and fulvic acid fractions of humic substances is part of the early stage of diagenesis. Diagenesis is any process affecting the products of primary production, which takes place prior to deposition and during the early stages of burial under conditions of relatively low temperature and pressure. The type of plant life and the microorganisms involved strongly affect the type of organic compounds that ultimately are preserved in sediments. Consequently, humic substances have widely varying chemical compositions and molecular weights (Ref. 18). These substances are generally acidic and are considered to be polymeric in structure. Concentrations of humic material in fresh waters are typically in the range of 1 to 10 mg/L (or ppm) as dissolved organic carbon (Refs. 19 and 20) and

in groundwaters, values of 2 to 4 mg C/L were reported in an early study (Ref. 21) while more recent work indicates values ranging from 0.2 to 15 mg C/L with average values in the range of 1 to 2 mg C/L.

Humic materials are operationally separated into two water-soluble fractions: fulvic acids and humic acids. The difference between these two groups is a result of varying molecular-weight ranges, solubilities, and the separation procedure used. The fulvic acid group has a lower molecular-weight range and a higher water solubility. Chemical analyses have consistently demonstrated the presence of a large fraction of aromatic, carboxylic acid, and phenolic functional groups in humic materials.

The aromatic nature of humic materials is noted by the strong absorbance of light in the UV wavelength range. The absorbance of light in the UV range is of interest in understanding some of the chemistry in the Pit lake system. Section 3.4 of the MWTP Activity IV, Project 8 Work Plan is investigating the effect light has on the iron(II)/iron(III) speciation (Ref. 22). This work is focused on the direct interaction of light with the aqueous iron. Recent reports (Refs. 23 and 24) have demonstrated how humic material, in particular fulvic acids, affects the iron speciation in acid mine waters through photochemical-induced oxidation/reduction reactions.

Phenolic and carboxylic acid groups in the humic substances are considered the key functionalities for binding hydrogen and metal ions. Numerous studies have been done to examine the proton and metal-binding abilities of humic materials in fresh, estuarian, and marine waters (Refs. 25, 26, 27, and 28). The results of these works have demonstrated the strong binding ability humic substances have for the hydrogen ion and certain other metal ions, e.g., copper, lead, and iron. It is unknown how humic substances may affect the Pit lake chemistry or metal transport. Work by

others has demonstrated that in natural water systems, the organic matter from humic substances is slowly remineralized as it sinks to lower depths (Ref. 29). It is possible that some inorganic carbon found in the deep Pit lake water is the result of the remineralization of humic substances. The remineralization of the humic material may result in a release of any bound metal ions, thereby recycling the metals into the water. Alternatively, entrapment of the metal ions may occur, removing them from the water through precipitation.

2.2   Results and Discussion

2.2.1   Total Organic Carbon
Personnel from the MBMG (Ref. 30) sampled the Berkeley Pit lake twice during this study. Samples were acquired from three separate sites on the Pit lake during November 1997 and from a fourth site during May 1998. Sites for the sampling are shown approximately on the map in Figure 2-1A. The organic carbon measurements for the samples collected during the fall of 1997 were determined on the Montana Tech of the University of Montana (Montana Tech) campus using a Shimadzu Corporation, Model TOC-5000A, Total Organic Carbon (TOC) Analyzer. Some samples collected during the spring of 1998 were analyzed using this same instrument. However due to instrument problems, the spring samples were eventually sent to a commercial laboratory for analysis. The TOC instrument was calibrated as suggested by the manufacturer using potassium-hydrogen-phthalate as the primary standard for organic carbon and sodium carbonate as the primary standard for inorganic carbon. An external calibration procedure was used. Filtered, deionized [18 megohms (MO)] water was used as the solvent for the calibration standards and as the blank.

Analyses of the fall 1997 samples were completed by measuring the total carbon (TC) and the inorganic carbon (IC). The TOC was determined as the difference between TC and IC. Total carbon is determined by injecting the aqueous sample into a heated, catalytic combustion tube where inorganic and organic forms of carbon are converted to carbon dioxide gas. The carbon dioxide is carried to the detector by the flow of combustion gas (air or oxygen) through the instrument. The detector is a nondispersive infrared (IR) absorption detector that measures the amount of light absorbed in the mid-IR range of the electromagnetic spectrum. The results of the analyses for the three sampling sites from November 1997 are given in Tables 2-1, 2-2, and 2-3 and Figure 2-2.

The three depth profiles are different in actual concentrations; however, there are some similar trends. Organic carbon content initially decreases with depth in the range of 2 to 25 feet. Then there is a sharp increase in the organic carbon concentration followed by another decrease in concentration with depth. Concentrations remain relatively constant in the 50- to 100-foot-depth ranges. Site 3 was not sampled beyond the 100-foot depth. Sites 1 and 2 show a second increase in organic carbon concentration in the 200- to 300-foot ranges. However, it is uncertain whether the concentrations of these deep samples are valid. Uncertainties (random and systematic error) in the determination of the TC and the IC are combined in the determination of the TOC since the TOC is determined by the difference between the TC and the IC values (Ref. 31). The TC and IC values become relatively large (20 to 30 mg C/ L) below 50 to 100 feet, and the difference between these values is small (5% to 20% of the TC value). It is reasonable to believe the error in the TOC values of the deep samples is nearly as large as the values. This belief is supported by the results from the May 1998 sampling where analyses of duplicates, matrix blanks, and spikes were performed to obtain an estimate of accuracy and precision of work. For example, using the interval at the 95% level, as determined for the 100-foot sample, the TOC value for the 300-foot sample in

Table 2-2 could vary from 1.42 to 4.42 mg C/L. Consequently, the TOC method of analysis was changed for the May 1998 sampling.

In addition to the analysis method, there was some concern in the sampling and storage of the water samples prior to analysis. The samples were stored in HDPE bottles, and some plastic lines were used in the sampling apparatus. These two sources of plastic could cause a contamination of the water with organic plasticizers. Potential sampling and storage problems for the November 1997 samples were addressed in the work performed on the May 1998 samples.

A few of the deep-water samples collected in May 1998 were analyzed at Montana Tech with the improved TOC method. The water samples were treated with concentrated phosphoric acid to convert IC (carbonate) to carbon dioxide and then sparged to remove the carbon dioxide from the water. The remaining carbon is often referred to as nonpurgable organic carbon (NPOC). However, in this report the NPOC will not be used; results will continue to be termed TOC. Due to problems with the use of the TOC instrument at Montana Tech, the samples collected in May 1998 and some that were collected during the summer of 1998 were analyzed by ACZ Laboratories, Inc. (ACZ), a commercial laboratory for chemical analysis (Ref. 32). The method used by ACZ was similar to that used for initial analyses at Montana Tech for the May 1998 samples.

Results from the analyses by ACZ for the May 1998 sampling of the Berkeley Pit lake at Site 4 are given in Table 2-4. There are two columns of TOC concentrations for each depth. The first concentration column shows the results as reported by ACZ. The concentrations of TOC in the water from the Berkeley Pit are near the detection limit of the method used by ACZ. The quoted detection limit from ACZ is 1 mg C/L, and the practical quantitation limit is 5 mg C/L.

Consequently, ACZ's results are considered accurate to 1 mg C/L. However, it was noted in preliminary sample analyses (performed at Montana Tech using a higher sensitivity method) that the changes in TOC concentration were small with changes in depth. Therefore, the second concentration column was used in producing a carbon depth profile at Site 4. Values in the second column are the ACZ results prior to them being rounded off to the unit mg C/L level. Figure 2-3 shows a plot of the TOC results (second concentration column) as a function of depth in the Pit lake.

There appears to be a significant amount of scatter in the data plotted in Figure 2-3. A portion of the scatter is real and results from the carbon concentrations being near the detection limit of the method. What appears to make the scatter so large is the small scale for the concentration axis. The difference between the largest and smallest concentrations is slightly more than 1 mg C/L. Data in Figure 2-3 shows a slight increase in the amount of organic carbon with depth. This trend is opposite that which was found in the fall of 1997. If the change in carbon concentration with depth is valid for the May 1998 results, the difference in the trends may be due to the differences in the environmental conditions, such as water and air temperature, hours of direct sunlight, etc. Differences in the absolute amount of TOC are also noted between the fall and spring samplings. A portion of this difference may be real; however, it is expected that the largest fraction of the difference is due to the Pit lake water matrix effect. The matrix effect is discussed in Section 2.2.2.

An initial concern was the possible contamination of water samples from sampling lines and equipment and the plastic storage bottles used for the November 1997 samples. The plastic sampling lines were replaced with Teflon lines for some of the May 1998 sampling. The Teflon lines created a problem in the actual sampling; therefore, a

limited number of samples were collected through the Teflon lines. A comparison of the two sampling lines, plastic versus Teflon, can be made using the data in Table 2-5.

The limited results in Table 2-5 show that sampling through the Teflon lines produced higher TOC results each time. However, the replicate analyses for the 100-foot sample acquired through the plastic line show a larger difference than that shown between the plastic and Teflon samples from the 50-foot samples. These results indicate that sample contamination from the plastic tubing is not detectable. The May 1998 sample from the 888-foot depth was collected in both glass and plastic bottles. The results from the TOC analysis on the Shimadzu instrument are given in Table 2-6. Multiple analyses of each sample were made, allowing for a statistical comparison of the results.

Results from a single sample indicate that the sample in the glass container contained a higher amount of TOC than the same sample in the plastic container. Using the t-test, these results are statistically different at the 95% confidence level. It is unknown why the analysis of the sample in the glass bottle produced such a high TOC value. However, at the time of sampling, the 888-foot level was near the bottom of the Pit. It is possible that some small colloidal material was collected in the one sample bottle and not the other. The glass bottles were purchased precleaned for the analysis of organic compounds in water. It is unlikely, but possible, that the glass bottle was contaminated. It should also be noted that the TOC results in Table 2-6 are higher than those reported in Table 2-7 for the same sample. The two sets of results were determined on different instruments, and as discussed in Section 2.2.2, are probably affected differently by the Pit lake water matrix.

From only a few analyses, data indicates that sample contamination did not occur from sampling lines or the plastic bottles used during the

November 1997 study. The liquid-liquid extraction and gas chromatography/mass spectrometry (GC/MS) results reported in Section 2.2.3 support this conclusion.

To determine the reproducibility of TOC analyses, four duplicate samples were sent to ACZ for analysis. The duplicates were chosen to cover the depth range of the Berkeley Pit lake at Site 4 and included the samples at the 20-, 100-, 200-, and 700-foot depths. In addition, ACZ did a duplicate analysis in each group of samples that were analyzed. The samples were divided by ACZ into three groups for analysis purposes. It was fortuitous that ACZ chose to analyze the 100-foot depth sample as one of their duplicates. The results from these duplicate analyses are given in Table 2-7. The results from the samples acquired through the Teflon tubing are not included in this data set.

The standard deviation (S) for the three analyses of the 100-foot sample is S=0.14. The relative standard deviation for these analyses is 3.2%. A confidence interval was calculated at the 95% confidence level and was determined to be $CI_{95\%}=0.35$. These statistical parameters can be used as an estimate for the precision of the results from the other samples.

2.2.2 Pit Lake Water Matrix Effect

From the early work on the November 1997 samples, it was suspected there was an interference in the TOC analyses. Subsequent analysis of TOC standards in the presence and absence of high concentrations of sulfate gave differing results. The presence of high sulfate concentrations always produced higher TOC results. Table 2-8 contains TOC results from the analyses of a deionized (DI), filtered (18 MO) water blank and a sodium sulfate solution made using the DI water. The sulfate concentration was 8,000 mg SO_4^{2-}/L.

The matrix effect is the result of the detection

system used in the TOC analyses. The TOC instrument used by ACZ and the Shimadzu instrument at Montana Tech uses nondispersive IR detectors. These detectors are responsive to any substance that will absorb light in the mid-IR region of the electromagnetic spectrum. Since the detector does not discriminate, any substance that absorbs light in this region will be recorded as coming from carbon.

Using the mean values in Table 2-9, the 8,000-mg/L sulfate solution (from sodium sulfate) produces a signal equivalent to 0.733 mg C/L of TOC. Two samples were analyzed by ACZ that contained 9,600 mg sulfate/L, one as ferrous (iron II) sulfate and the other as ferric (iron III) sulfate. The ferrous sulfate solution was prepared by dissolving 0.9850 grams (g) of clean, pure iron wire in 10.2 g of concentrated sulfuric acid, a few milliliters of concentrated nitric acid to oxidize the iron metal to iron (II), and enough DI water to bring the final volume of the solution to 1 L. The ferric sulfate solution was prepared by adding a stoichiometric excess of hydrogen peroxide to an aliquot of the ferrous sulfate solution. Results from the TOC analyses of the three sulfate solutions are given in Table 2-9. The values listed in Table 2-9 have been corrected for the instrumental blank.

A direct comparison cannot be made between the result obtained on the Shimadzu TOC and the results from ACZ since the two instruments used are different. However, the apparent detection of organic carbon by two different laboratories using two different instruments for noncarbon-containing compounds substantiates the concern of a matrix effect from the Berkeley Pit lake water on the TOC analysis. A second potential problem appears in the difference between the ferrous and ferric sulfate results. If these results can be substantiated by additional analyses, then it will be necessary to correct the TOC results based on the sulfate concentration and the relative amounts of iron(II) and iron(III). Additional work will be

carried out to verify the results presented above.

To determine the cause of the matrix interference, the gas produced in the catalytic combustion cell of the TOC was collected and analyzed using a dispersive IR spectrometer. The gas passing to the detector of the Shimadzu TOC was collected cryogenically using a coiled copper tube submerged in liquid argon. Liquid argon was used as the coolant because it was readily available, and its boiling point (-185.7 EC) is close to that of oxygen (-182.96 EC). It was hoped that most of the oxygen in the gas stream would pass through the tube without being condensed. Oxygen is used in the combustion of organic carbon to carbon dioxide and to transport

the carbon dioxide to the TOC detector. Oxygen gas is transparent in the mid-IR region of the spectrum and is therefore not detected by the TOC instrument. However, oxygen should be the major component of the gas stream and could fill the copper tube, if it condensed, and prevent the collection of any other gases. Water vapor and hydrogen chloride, both light absorbers in the mid-IR range, are removed prior to the gas entering the TOC detector. The water sample from the 888-foot depth was injected 30 times into the TOC instrument to produce gas for the analysis with the dispersive IR absorption spectrometer.

The volume of the sample cell in the dispersive instrument is several orders of magnitude larger than that of the TOC instrument. Consequently, the magnitude of the signal in the dispersive instrument is reduced accordingly. However, three discernable peaks are noted in the spectrum. The peak centered at 2,305 wave numbers (cm) is from carbon dioxide. The carbon dioxide is the combustion product of the organic carbon in the water sample. The appearance of two peaks at approximately 1,335 and 1,365 cm correspond to sulfur dioxide and sulfur trioxide, respectively.

The IR results and the sulfate salts analysis results

indicate the sulfate is decomposing in the combustion tube to generate sulfur-oxide gases. The sulfur oxides are detected by the nondispersive IR detector, and the resulting signal is combined with that from any carbon dioxide generated from organic carbon. The TOC analysis of the Berkeley Pit lake waters must be corrected for sulfate interference. However, as seen by the data in Table 2-9, the sulfate correction may be dependent on the type of metals and the oxidation state of the metals in solution with the sulfate. Additional work must be done to identify the magnitude and the conditions of the matrix interference
more accurately.

2.2.3 Determination of Organic Carbon Sources

As discussed in Section 2.1, there are several potential sources for organic carbon in the water of the Berkeley Pit lake. The most likely sources are petroleum hydrocarbons from fuels or lubricants, microorganisms living in the Pit lake, and naturally occurring organic matter brought by the in-flow water. Some preliminary studies were done to determine which of these sources might contribute to the organic carbon in the Pit water.

Volatile Fuel Hydrocarbons

A liquid-liquid extraction procedure combined with GC/MS was used to analyze for volatile organic compounds. The extraction was a modified Soxlet extraction, and methylene chloride (CH_2Cl_2) was used as the extraction solvent. The CH_2Cl_2 was bubbled through the water by heating, then condensed and allowed to percolate back through the water. Organic compounds, such as those found in fuels and some lubricants, are highly soluble in CH_2Cl_2 and will be extracted from the water layer. The extraction solution was concentrated in a Kuderna-Danish (K-D) concentrator. Deionized water was extracted using this process and used as a blank. The extraction process was then used on the Berkeley Pit lake water sample acquired at the depth of 888

feet. The sample was stored in an amber glass bottle at 4 EC prior to extraction. Medium-grade unleaded gasoline (1 mL) was mixed with 100 mL of DI water. This produced a saturated solution of the gasoline in water and had a concentration of approximately 500 mg C/L. An aliquot of this mixture was extracted using the process described above. Some of the results from these two analyses are shown in Figures 2-4 and 2-5.

The chromatogram in Figure 2-4 is from the extract of the Berkeley Pit lake water acquired at the 888-foot depth. The small peaks seen in the 6- to 10-minute timeframe are also found in the extract from the DI water. These small peaks are caused by a buildup of contamination (high molecular weight, nonvolatile compounds) in the GC and are considered instrumental background.

The chromatogram in Figure 2-5 is from the extract of DI water that was saturated with gasoline (approximately 500 mg C/L). The large number of peaks in the GC result from the hundreds of compounds that constitute gasoline. The most intense peaks are produced from the substituted aromatic compounds. A comparison of the chromatograms in Figures 2-4 and 2-5 indicates that if fuels (gasoline or diesel) are present in the water, the fuel concentration is less than 1 mg C/L.

The presence of organic carbon from fuels in the Pit lake water has not been eliminated. The concentration of this material, if present, is probably small relative to the TOC concentration. Additional work should be done to investigate the possibility and extent of fuel material in the water. This work should include the extraction of significantly larger volumes of water to obtain a larger concentration factor. Water from several different depths should also be extracted.

Microbes and Colloids

Microbes and large colloids can be removed from water by filtering or centrifugation; both of these

methods were used to determine if the TOC, or some sizable fraction of the TOC was from microbes or colloidal material. Total organic carbon analyses of filtered and unfiltered Pit lake water samples from the November 1997 sampling showed no statistical difference.[4] Using samples collected during May 1998, sample tubes were filled with 50 mL of Pit lake water and centrifuged using a procedure developed by Mitman.[5] This procedure produced white solids from shallow water samples acquired near Pit benches. The samples used in this work were collected at 5- and 10-foot depths and stored in plastic bottles; samples from the 1- and 715-foot depths were stored in glass bottles. The sample bottles were thoroughly shaken prior to water being poured into the centrifuge tubes. The tubes were spun for 2 minutes, reaching a maximum speed of 1,200 revolutions per minute (rpm). The tubes were then removed from the centrifuge and inspected for the presence of solid; no solid was detected. The centrifugation was repeated using a spin time of 5 minutes with a maximum speed of 2,050 rpm. Again, no solid was detected. The tubes were covered with aluminum foil and placed in a cooled incubator overnight; no solid was detected. The tubes were spun one more time for 10 minutes with a maximum speed of 2,700 rpm; no solids were detected. The TOC analysis of these samples was not done due to instrumental problems. It is assumed, from the absence of solid produced by centrifugation, that microbiological organisms contribute an insignificant amount to the TOC values from the bulk Pit lake waters.

Naturally Occurring Organic Matter
The most likely source for the organic carbon in the Pit lake water is from the inflow water. This idea is substantiated by the analysis of well water that feeds the Berkeley Pit and surface water that previously flowed into the Pit. The TOC values from these feed waters, in addition to values from a few wall seeps (springs), are given in Table 2-10.

Samples from site numbers x,y, z, and qq are waters that are flowing to or historically had flowed to the Berkeley Pit. The sampling sites are shown on the map in Figure 2-1B. These waters show TOC values in the range of 1.62 to 2.32 mg C/L. These concentrations are typical of TOC values for natural waters, although they are high-end values for groundwaters. The remaining sample sites (Figure 2-1A) in Table 2-10 are spring (seep) sites in the Pit walls and have TOC concentrations similar to those of the Pit lake water. These seep waters are expected to be high in sulfate concentration and consequently have a matrix interference in the TOC analysis similar to the Pit lake water. The results from Table 2-8 suggest the sulfate concentration will contribute approximately 0.7 to 1.5 mg C/L to the TOC results. Using the high end of the interference range, the in-flow water is similar in TOC concentration to that found in the Berkeley Pit lake water. Consequently, one would expect the carbon distribution in the Berkeley Pit lake water to be similar to that found in natural waters. Table 2-11 contains average organic carbon-type distributions for natural waters (Ref. 16).

The results in Table 2-11 indicate that in natural waters the humic materials (fulvic and humic acids) make up the largest fraction of organic carbon, approximately 50%. Hydrophilic acids are similar to the fulvic acids; however, the hydrophilic acids are generally lower in molecular weight and higher in aqueous solubility. The hydrophilic acids can also bind metal ions and participate in a variety of photochemical reactions.

Experiments were performed to separate humic matter from the Berkeley Pit lake water. Amberlite XAD-2 resin was packed into a column

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[4]William Chatham, Chemistry and Geochemistry Dept., Montana Tech of the University of Montana, personal communication, 1998.

[5]Grant Mitman, Biology Dept., Montana Tech of the University of Montana, personal communication, 1998.

and used to remove the humic substances. The separation procedure was tested using a standard humic acid from Aldrich dissolved in DI water. The water was acidified to a pH of 2 with hydrochloric acid. Figure 2-6 contains the UV/visible (VIS) absorption spectra for a 5-mg C/L solution of the standard humic acid before and after the solution was run through the XAD-2 filled column. From these spectra, it is observed that an efficient extraction of the humic material from DI water is possible.

The UV/VIS absorption spectrum of Berkeley Pit lake water from a depth of 1 foot at Site 4 appears quite noisy (large fluctuations) at the peak maximum between 200 and 400 nanometers (nm). The instability of the signal results from nearly all the light being absorbed at these wavelengths. This strong absorption is due to the large concentration of iron in the water. A ten-fold dilution of this sample with DI water was performed. The majority of the absorption signal from this sample is also due to the iron in the solution. It is obvious that a direct determination of the humic substances in the Pit lake water is not possible using this method. The Pit lake water was run through the XAD-2 column to extract the humic material. Unfortunately, the iron in the solution strongly sorbed to the resin, turning the resin a yellow-brown color. The UV/VIS absorption analysis of the effluent determined that a high concentration of iron was still remaining in the water. The iron absorption on the column resin masked any absorption of the humic materials. A basic eluant was run through the column to remove any humic material that might be absorbed in the resin. The UV/VIS absorption analysis of the column effluent did not detect any humic material. This result was not unexpected since the extraction column was so contaminated with iron. It is necessary to develop a different extraction procedure to analyze for the humic materials in the Pit lake water. A procedure similar to that used to remove humics from soils is currently being developed and tested (Ref. 33).

2.3 Conclusion

Multiple analyses of water from different locations and depths in the Berkeley Pit have confirmed the presence of organic carbon. The amount of organic carbon as measured by a nondispersive IR spectroscopic absorption analysis varies from 3 to 5 ppm (mg C/L). There is a slight variation of the organic carbon concentration with depth. However, the carbon depth profile changed between the fall 1997 and spring 1998 samplings. It is not known if this change is real or an artifact of the analysis methods used.

Analysis of blanks, standards, and spikes determined that the high sulfate concentration in the Pit lake water created an interference in the TOC analysis. The sulfate is decomposed within the instrument to sulfur oxides. The sulfur oxides are not distinguished from carbon dioxide, which is the combustion product and marker compound for the quantification of the organic carbon. This matrix interference varied from 0.7 to 1.5 ppm, measured as mg C/L. The variation in the matrix interference appears to be dependent, in part, on the metals in the water and their oxidation states.

The matrix interference results suggest that the true concentration of organic carbon in the Berkeley Pit lake water is in the range of 1.5 to 3.5 mg C/L. These latter values are similar to what is found in the water that is flowing into the Pit and suggest that the organic carbon is from natural sources. Filtration and centrifugation separations indicate that living microorganisms do not account for a measurable amount of the TOC in deep waters and water away from the Pit lake. Liquid to liquid extractions of Pit lake water followed by GC/MS analysis did not detect any fuel-type hydrocarbons at the ppm level. This result is supported by the results indicating that the organic carbon found in the Pit lake water is from natural sources.

Additional work needs to be performed to quantitate the matrix effect and determine which water quality parameters affect the magnitude of

the matrix effect. Development of better methods to separate and analyze the organic carbon in the acidic mine wastewaters of the Berkeley Pit is also necessary. The high acid, metal ion, and sulfate concentrations adversely affected the methods to determine the type and amounts of different organic materials present in the Pit lake water.
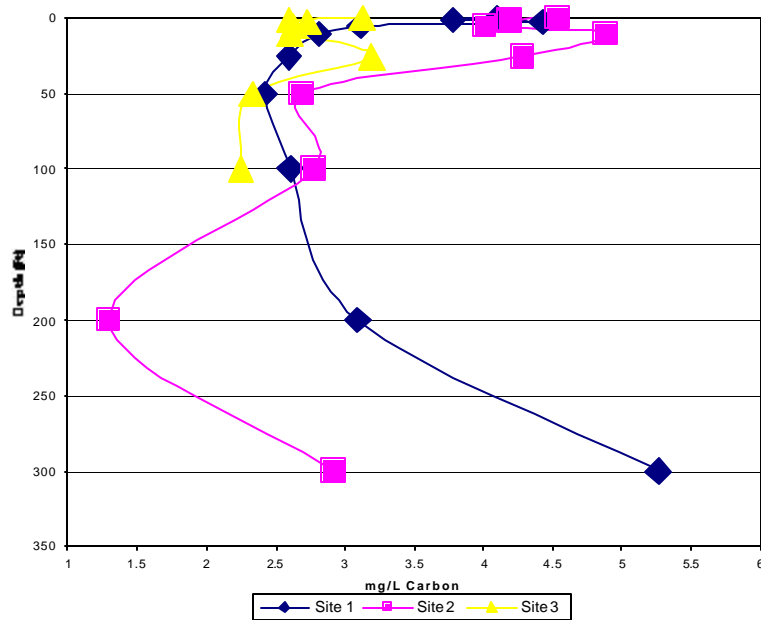
Figure 2-2. TOC with depth at Sites 1, 2, and 3 in the Berkeley Pit lake, November 1997 sampling.
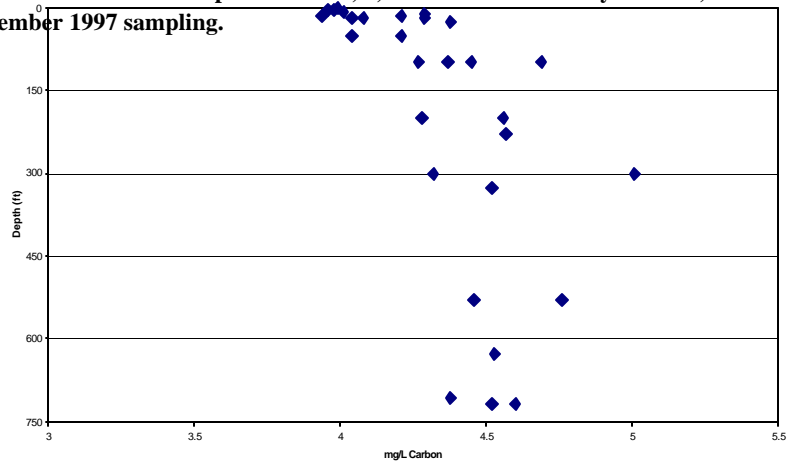
Figure 2-3. TOC with depth at Site 4 in the Berkeley Pit lake, May 1998 sampling.

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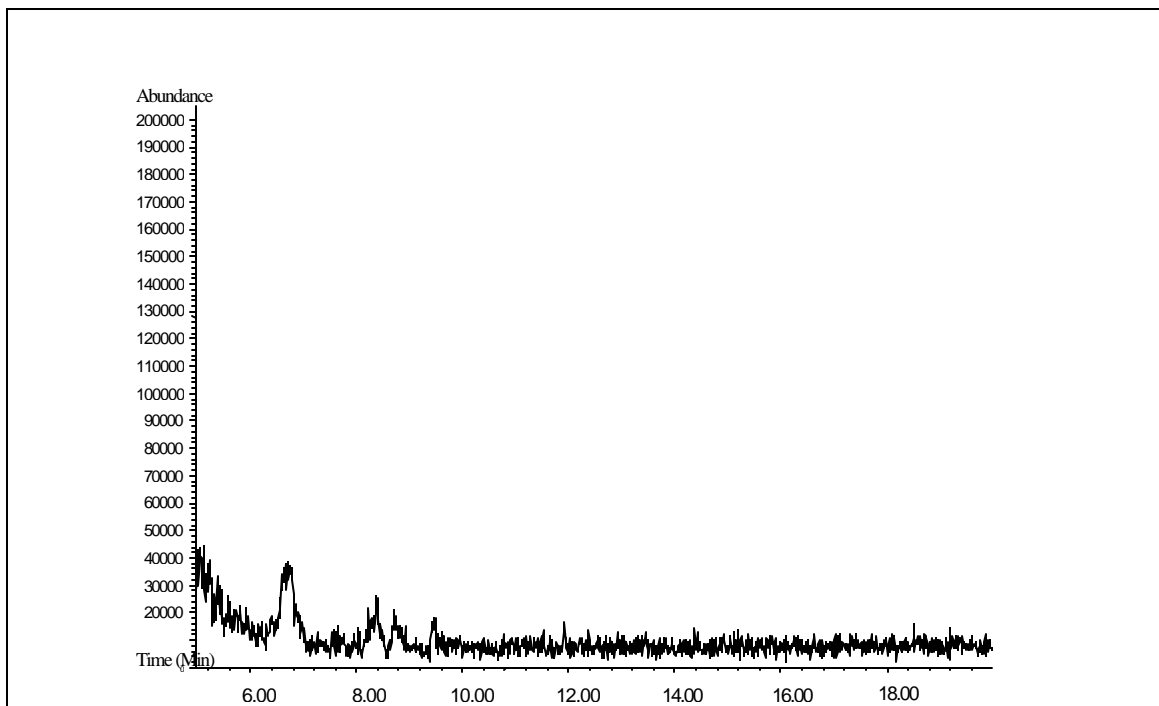
Figure 2-4. Chromatogram from the GC/MS analysis of a CH$_2$Cl$_2$ extract from Site 4 at the 888-foot depth.
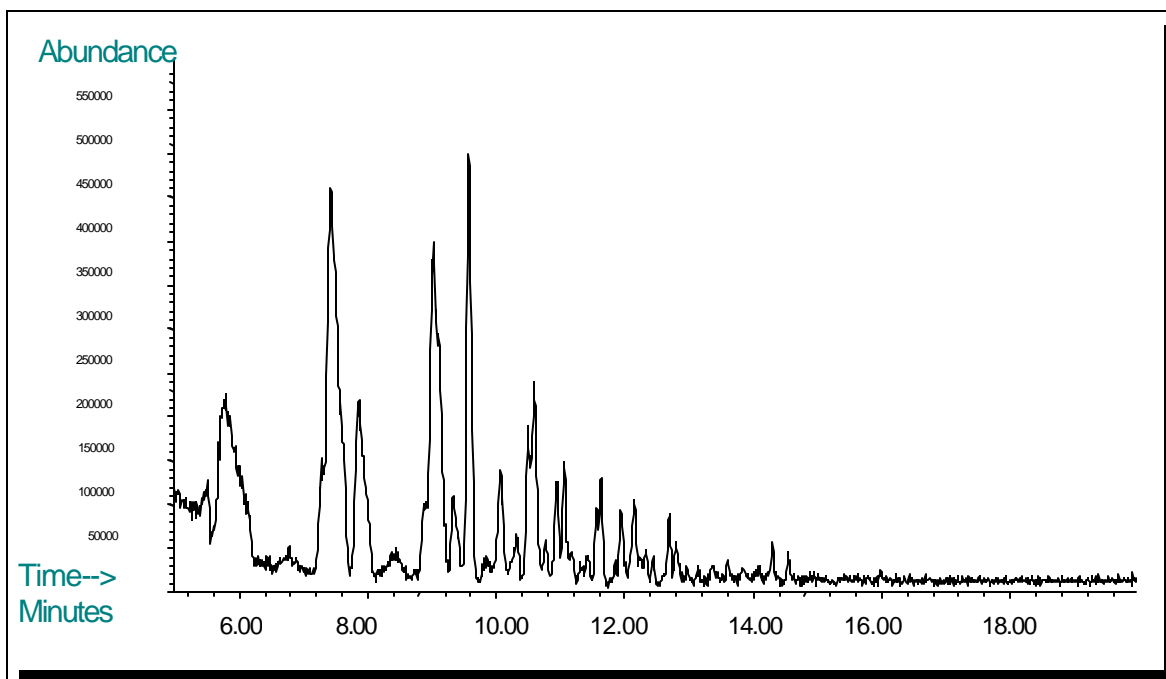
Figure 2-5. Chromatogram from the GC/MS analysis of a CH$_2$Cl$_2$ extract from DI water spiked with gasoline.

HUMIC ACID UV/VIS ABSORPTION SPECTRUM
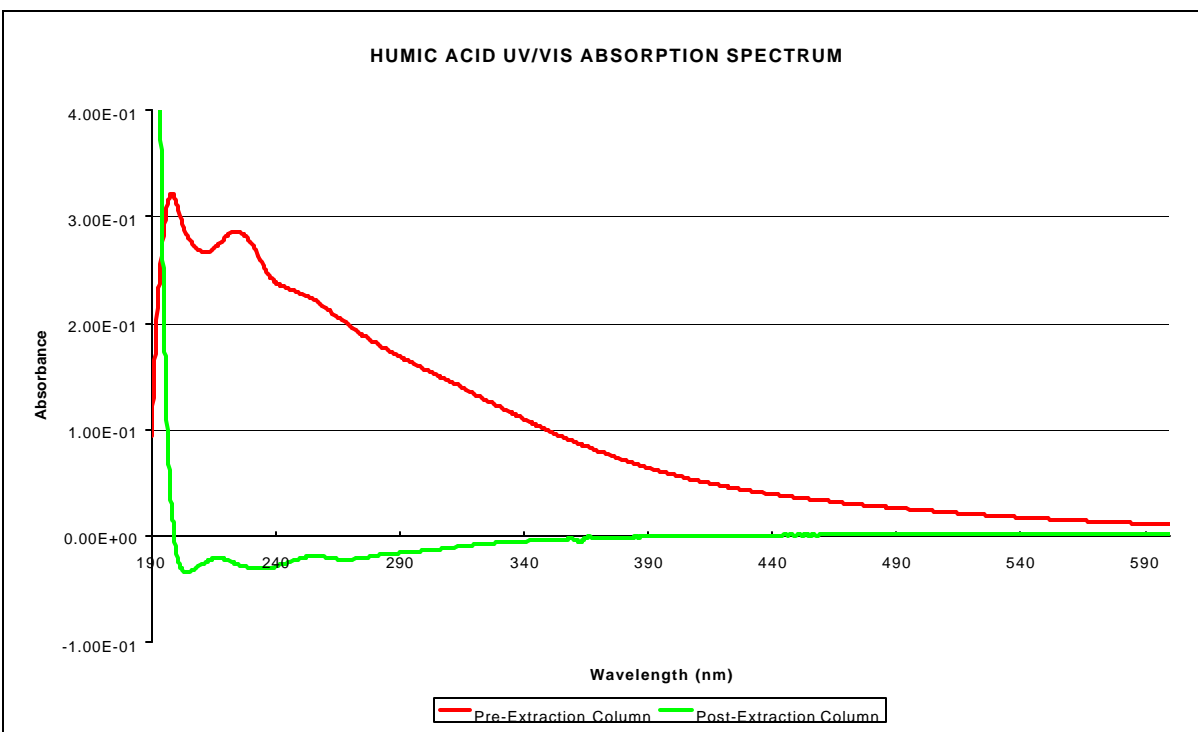
Figure 2-6. UV/VIS absorption spectra of 5-mg C/L standard humic acid solution before and after elution through a XAD-2 resin column.

Table 2-1. Carbon Concentration as a Function of Depth at Site 1

Depth	Total Carbon	Inorganic Carbon	Organic Carbon
(feet)	(mg C/L)	(mg C/L)	(mg C/L)
0.5	6.99	2.89	4.1
1	7.24	3.46	3.78
2	8.04	3.62	4.42
5	5.77	2.66	3.12
10	5.94	3.12	2.82
25	6.19	3.59	2.6
50	21.46	19.03	2.43
100	31.14	28.53	2.61
200	28.13	25.04	3.09

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| 300 | 30.84 | 25.57 | 5.27 |

Table 2-2. Carbon Concentration as a Function of Depth at Site 2

Depth (feet)	Total Carbon (mg C/L)	Inorganic Carbon (mg C/L)	Organic Carbon (mg C/L)
0.5	7.36	2.82	4.54
1	7.36	3.15	4.2
2	7.7	3.51	4.19
5	8.45	4.44	4.01
10	6.75	1.87	4.88
25	7.06	2.76	4.29
50	27.83	25.14	2.69
100	19.82	17.04	2.78
200	26.99	25.69	1.3
300	24.86	21.94	2.92

Table 2-3. Carbon Concentration as a Function of Depth at Site 3

Depth (feet)	Total Carbon (mg C/L)	Inorganic Carbon (mg C/L)	Organic Carbon (mg C/L)
0.5	5.37	2.24	3.13
1	5.57	2.97	2.6
2	4.83	2.1	2.74
5	5.86	3.23	2.63
10	4.55	1.94	2.61
25	5	1.81	3.19
50	16.16	13.83	2.33
100	18.72	16.47	2.25

Table 2-4. TOC Concentration as a Function of Depth at Site 4, May 1998

Depth (ft)	TOC (1) (mg C/L)	TOC (2) (mg C/L)	Depth (ft)	TOC (1) (mg C/L)	TOC (2) (mg C/L)	Depth (ft)	TOC (1) (mg C/L)	TOC (2) (mg C/L)
0.5	4	3.99	20	4	4.04	300	4	4.66
1	4	3.96	25	4	4.21	400	4	4.52
2	4	3.98	50	4	4.27	500	5	4.76
4	4	4.01	50	4	4.37	600	4	4.46
6	4	4.29	100	4	4.45	700	4	4.53
8	4	3.94	100	5	4.69	700	4	4.48
12	4	4.21	100	4	4.28	800	5	4.38
14	4	4.04	100	4	4.56	880	5	4.52
16	4	4.08	200	4	4.32	885	4	4.6
18	4	4.29	200	5	5.01	888	5	4.85
20	4	4.38	300	4	4.57	888	5	4.62

ACZ results rounded to the unit value of mg C/L.
ACZ results rounded to the hundredth value of mg C/L.

Table 2-5. Comparison of TOC Results Through Plastic and Teflon Sampling Lines

Sample ID (*)	Mg C/L
50P	4.27
50T	4.37
100P	4.28
100P	4.45
100T	4.69

(*)The value indicates the depth from which the sample was obtained. "P" indicates plastic lines and "T" indicates Teflon lines.

Table 2-6. TOC from Sample 888-In Glass and Plastic Bottles

Container	mg C/L	Standard Deviation
Plastic	5.197	0.652

Glass   6.122   0.498

**Table 2-7. Duplicate TOC Analyses from Site 4, May
1998**

Sample Depth (ft)	mg C/L
20	4.04, 4.38
100	4.28, 4.45, 4.56[1]
200	4.32, 5.01
300	4.57, 4.66[1]
700	4.48, 4.53
888	4.62[1], 4.85

These values are from the duplicate analyses determined by
ACZ.

**Table 2-8. TOC Signal from DI Water Blank and Sodium Sulfate
Solution**

Analysis Number	DI Water (mg C/L)	Na_2SO_4 Solution (mg C/L)
1	0.643	1.328
2	0.584	1.325
3	0.566	1.232
4	0.420	1.194
5	0.362	1.294
6	0.509	1.074
7	0.539	1.304
Mean	0.517	1.250
Standard Deviation	0.097	0.092

Table 2-9. TOC Signals from Three Sulfate Solutions

Sulfate Type and Concentration mg/L	Signal as mg C/L
Sodium Sulfate (8,000)	0.733
Ferrous Sulfate (9,600)	1.56
Ferric Sulfate (9,600)	0.79

Table 2-10. Total Organic Carbon at Various Sites Around the Berkeley Pit Lake

Site Location	TOC [1] (mg C/L)	TOC [2] (mg C/L)
N.E. Spring	2	2.22
South	4	4.32
North Wood	3	3.74
E. Haul Rd Spring	4	4.53
North Spring	2	1.82
North	4	4.24
Silver Bow Cr.	2	1.62
Upper Yankee	2	2.32

1 ACZ results rounded to the unit value of mg C/L.
2 ACZ results rounded to the hundredth value of mg C/L.

Table 2-11. Relative Amounts of Organic Carbon Compound Types in Natural Waters

Carbon Compound Type	Relative Amount Carbon Compound Type
Fulvic Acid	40%
Humic Acid	10%
Hydrophilic Acid	30%
Carbohydrates	10%
Simple Carboxylic Acids	6%
Free Amino Acids	3%

Hydrocarbons   1%

3. Sulfate-Reducing Bacteria Activity in the Berkeley Pit Lake System

The goal of this research is to survey the Berkeley Pit for microorganisms, specifically looking for sulfate-reducing bacteria (SRB). Bacteria are present in the Berkeley Pit water but in numbers considered below normal for surface water. While bacteria have cultured well, they have thus far proven resistant to isolation. Fungi, on the other hand, have cultured and isolated well; three organisms have been identified.

3.1 Background

The Berkeley Pit is the largest Pit lake in the United States. An abandoned open-pit copper mine located in Butte, Montana, the Berkeley Pit continues to fill with water. Due to the oxidation of pyrite in the bedrock, the resulting lake is acidic: low pH and heavy metals with high concentrations in solution. In conjunction with the treatment goal for the Pit water, new technologies are being developed and tested in hopes of minimizing the cost, or showing a profit by economically mining the metals out of solution.

In addition to treatment technology development, basic research is being conducted to better understand the unique features of the Berkeley Pit lake. This section reports on the study of the biological activity of the Berkeley Pit. Prior to this study, very little was known about the ecology of the Berkeley Pit lake.

The SRB can be considered a physiological unified group of bacteria that consists of dissimilatory SRB placed into 18 genera. These genera of bacteria are physiologically separated into four further subgroups depending on their carbon source (nonacetate oxidizers, acetate oxidizers, dissimilatory sulfur reducers, and hyperthermophilic Archaea). Sulfate-reducing bacteria chemically reduce sulfate to sulfide using sulfur as the terminal electron acceptor and use

organic acids, fatty acids, alcohols, carbon dioxide, and hydrogen (H_2) as electron donors, all under anaerobic conditions. As a result of this process, a number of beneficial results may occur with respect to bioremediation.

C These organisms naturally raise the pH of the acidic solutions in which they are growing by various physiological processes.

C They are major consumers and decomposers in the food web.

C These microbes play a role in the biological magnification of toxic materials (each trophic level of the food web will increase the concentration of many metals 10 times).

C Heterotrophic microbes are important in biogeochemical cycling of carbon, nitrogen, phosphorus, sulfur, and other elements—most importantly in nitrogen fixation and sulfate reduction.

C Some microbes have metalothionines—detoxifying enzymes that may have a synergistic effect on the microbial community.

C Biomass accumulation and eventual decomposition will not only increase the organic carbon component of mine waste systems but will also promote heterotrophic growth of other bacteria, fungi, and protozoans.

C Heterotrophic microbes will release bound nutrients during decomposition—the microbial loop model (Ref. 34).

These combined physiological processes of microbiota have been observed to bioremediate

aquatic mine waste environments (Ref. 35). Consequently, if a mine waste site, like the Berkeley Pit lake system, is properly nutrified with nitrogen, phosphorous, potassium, e.g., aged manure or sewage as inexpensive sources, or a carbon source, then this nutrification may cause a successional cascade of increased diversity and biomass that is coupled with an increase in pH. A pH increase, in turn, may lead to a natural restoration process. Thus, if systems are to function correctly and recover from pollution-induced perturbations, fundamental information both on the autotrophic and on the heterotrophic components of the microbial community is essential. Defining the baseline community structure is the first step not only toward understanding the interactions of the different groups of organisms but also toward assessing any improvement in biodiversity within the biotic community.

3.2   Objectives

This project had two principal objectives: 1) determine the baseline community structure of SRB in the Berkeley Pit lake; and 2) evaluate the isolated species for possible use in bioremediation. These two goals are necessary to gain a fundamental understanding of the microbial ecology of acid mine waste areas and to evaluate the potential of these organisms as bioremediators.

3.3   Methods and Materials

3.3.1   Sampling

The Berkeley Pit was sampled twice, once in the fall and once in the spring. The first sampling event occurred November 1997, and the second sampling occurred from April 22 to May 28, 1998. Six samples were collected April 22, three from a shallow depth (180 feet) and three from a greater depth (890 feet). At each depth, two water samples and one sediment sample were collected. From May 6 to 8, samples were collected with a vertical sampler at depths of 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 50, 100, 200, 227, 300, 327, 427, 527,

627, 707, 712, and 715 feet. On May 11, two grab samples were taken from a spring on the south side of the Pit, one of spring water and one of spring/Pit water. On May 28, 14 thin-layer samples were collected from the surface (0 to 4 feet), the thermocline (10 to 14 feet), and near bottom (707 to 711 feet). On the same day, the following grab samples were collected: northeast spring sediment, northeast spring water, north spring, northside wood near spring, and northside wood.

All sampling was performed by MBMG personnel. Water column samples were collected with a vertical sampler. The vertical sampler consists of a plastic tube with two doors held open at either end. When the vertical sampler is at the appropriate depth, a messenger weight is released down the line, tripping a lever allowing the two doors to securely close. Upon reaching the surface, the contents of the vertical sampler were transferred to quart-size mason jars with no head space. Water column samples were also collected with a thin-layer sampler. The thin-layer sampler consists of a frame with 11 syringes spread over a vertical distance of 4 feet. With the syringes held closed, rubber tubing is attached to the end of each syringe. Upon reaching the chosen depth, a messenger weight is released, triggering the release of the syringes. Syringes were capped on return to the surface.

3.3.2   Media

The original focus of this study was the cultivation, isolation, and identification of SRB. Thus, the first growth media used were specifically for SRB (Postgate Medium C and SRB Enrichment Medium). Many variations on the original Postgate Medium C were used. Concentrations of carbon sources were decreased to closely resemble the low nutrient level of the Berkeley Pit lake, and different carbon sources were used. Instead of 6 milligrams (mg) of lactic acid, 1 mg was used. Acetic, propionic, and butyric acid were substituted for lactic acid, and all four acids

were used together at a total concentration of 1 mg/L. Postgate C Medium was made both as a liquid (as directed) and as a solid with the addition of Bacto-Agar.

Postgate E Medium was made as directed. The SRB enumeration medium from standard methods was made as directed. Several media were made with filter sterilized Pit lake water to arrive at a medium more closely resembling the Pit lake. Media made with Pit lake water include Bacto-Agar, Nutrient Agar, and Postgate C. A *Thiobacillus* medium (ATCC Medium 125) was made for the cultivation of the acidophilic *Thiobacillus* organism.

3.3.3 Equipment

To hold liquid media, 20-mL and 40-mL EPA vials with silica septum were used. Solid media was poured into disposable petri dishes or test tubes. Inoculations or isolation streaks were made with disposable loops. Inoculation of all liquid media was made with syringes and size 18 needles. Inoculation of petri dishes was made with either syringes or pipettes. Anaerobic conditions were maintained with anaerobic jars. Jars were made anaerobic by inserting BBL anaerobic gas packs or by flooding the jar with filtered nitrogen gas. Working anaerobic conditions were maintained in a custom-made glovebox under positive pressure. Autoclaving was performed in the manual Market Forge Sterilmatic autoclave or the computerized Amsco Scientific SG-120 autoclave. Microscopy was done with the Nikon 800e. Fluorescent dyes used for bacterial counts of sediment samples were DAPI and Molecular Probes Live/Dead *Bac*Light.

3.3.4 Methods

Petri dishes were inoculated with liquid samples by adding 1 mL of liquid to the agar surface and tilting the dish to evenly distribute liquid over the surface of the agar. Vials were inoculated by first disinfecting the septum with alcohol and then injecting 1 mL of sample. Fluorescent dyes were

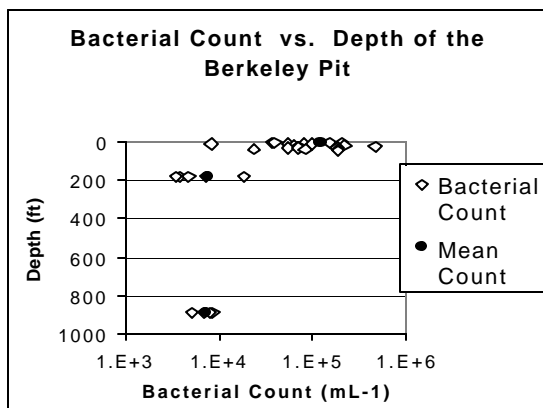used as directed by the manufacturers.

Isolation was attempted three ways: streaking, dilution, and solidification/entrapment. Streaking involved streaking a loopful of culture continuously back and forth across the agar surface in a petri dish. Dilution involved adding a loopful of culture to either sterile water purged with filtered nitrogen or to a liquid medium. A fraction of the inoculated liquid was then withdrawn and added to another vial of liquid; this was repeated until sufficient dilution was achieved. A fraction of each dilution was then withdrawn and used to inoculate solid medium in a petri dish. Solidification/entrapment included allowing a solid medium to cool after being removed from the autoclave. Prior to solidification of the medium, it was poured into test tubes, inoculated, and mixed with a vortex spinner. Upon solidification of the medium, wax was poured on top of the wax to seal the medium and prevent contamination.

3.4   Results

No SRB or any SRB activity was detected in the Berkeley Pit lake system. Earlier reports of SRB activity may have been in error, or possibly metabolically inactive bacteria were isolated by enrichment. Furthermore, the lack of black-reducing sediments and poor habitat conditions suggest that they may only exist as a refugia or microhabitat population, if at all. Researchers involved in this study have not been able to isolate any SRB from the Berkeley Pit lake system. Nevertheless, in this project's attempt to isolate SRBs, a variety of interesting fungi and yeasts were isolated. Bacteria, although present, are fastidious, and to date, no other researcher involved with this project has been able to successfully isolate SRB.

3.4.1 Bacterial Counts

Bacterial counts of sediment samples failed, while bacterial counts of the water column proved successful. Surface counts (0 to 35 feet) are from November 1997 samples; depth counts (180 and

Bacterial Count vs. Depth of the Berkeley Pit

Figure 3-1. Bacterial counts of the Berkeley Pit lake water column. Reported counts (mL^{-1}) are mean values.

890 feet) are from May 1998. Counts varied greatly; however, the generalization can be made of the water column that the bacterial population is greater at the surface (see Figure 3-1).

3.4.2 Culture, Isolation, and Identification of Microorganisms

Bacteria and fungi cultured well. Bacteria did best in the complex SRB medium. Little success was achieved with the simplest of media, Berkeley Pit lake water and Bacto-Agar. No growth was evident in the *Thiobacillus* medium.

Fungi isolated easily with the streaking method; 19 molds and 1 yeast were isolated. Bacterial isolation was attempted with all three isolation methods on all previously mentioned media; all bacterial isolation attempts failed. After each isolation attempt, the results have been one of two possibilities: no bacteria or a mixed culture.

Five samples, four molds, and one yeast were sent to MIDI Labs for identification using fatty acid analysis. The yeast was identified as *Candida famata*, and two of the molds were identified as *Exophiala moniliae* and *Botrytis spp*. The other two molds could not be identified and may be new

3.5 Discussion

Fungi cultured and isolated easily; however, nothing can be said of their activity in the Berkeley Pit lake. From the samples gathered, it can be said that the Berkeley Pit lake is not the best environment for SRB. In none of the samples collected was the E_H below 650 mV or the pH above 3.5. Optimum SRB growth occurs at a circumneutral pH and an E_H of roughly –200 mV. While SRB cultivation has not been confirmed through isolation, SRB are suspected to be present based on visual inspection. If SRB are cultured from the Berkeley Pit lake, they may be present as a dormant cell or as an active member of a microbial community.

While bacteria have cultured well, they have been resistant to isolation. There are several possible reasons for this lack of isolation, some of them routine (poor technique, contamination, etc.) but others specific to this project. Technique may have been a problem when the project began a year ago, but it is not seen as cause for current isolation problems.

The most likely possibility is that the bacteria are simply very fastidious. While they seem to culture well, the further they are removed from their environment during the process of isolation, the worse they may do. This is tied to the possibility that the correct medium may not have been employed. Sulfate-reducing bacteria media were originally used because SRB are the main bacteria of interest. The use of these media continued because the media appeared to work well culturing bacteria. Different media may be needed for successful isolation of whatever bacteria are in culture.

Another likely possibility is that some of the bacteria are very motile. While viewing mixed cultures under the microscope, several bacteria have been witnessed to be highly motile. This may

explain why some isolation attempts have resulted in a mixed culture.

One remote possibility is that syntropy is occurring. Syntropy is when the by-product of one bacterium is used by another bacterium to survive, thus isolation would kill the bacteria. Again, this is unlikely, but if proven, it would be a discovery in itself.

The possible motility problem would be dealt with effectively through the solidification/entrapment method. This method began recently, and results from this method are not yet complete.

Bacterial counts from the water column are low (approximately 100,000/mL). A count from a normal drop of water is around one million. The low numbers found in the Berkeley Pit lake are most likely a result of the carbon source limited nature of the Pit.

Bacterial counts of the sediment failed. The two fluorescent dyes used seemed to have a greater affinity for the sediment than the bacteria. Switching between brightfield and fluorescent microscopy, it was evident that the bacteria were not stained, but instead it was the sediment particles fluorescing.

3.6 Conclusions And Recommendations

Continued work needs to take place on the isolation and identification of Berkeley Pit lake bacteria. This should consist of continued testing of different media until one is found that isolates bacteria well. After an isolation method has been developed, sediment bacterial counts should be performed. While bacterial counts have been successful for the water column, a method must still be found for performing a count on sediment bacteria.

Fungi have cultured and isolated well, resulting in 19 isolates; 3 of the isolates have been identified: *Candida famata*, *Exophiala moniliae*, and *Botrytis spp*. Nothing can be said about the activity of the fungi in situ.

It should be stressed that this report is seen as a preliminary report due to the difficulty of isolating bacteria. This study is involved with a topic of which truly nothing is known: the microbiology of the Berkeley Pit lake. The lack of previous work provides no foundation from which to build. Work will continue on bacterial isolation and identification until April 1999. When bacteria isolation and identification are successful, an updated report will be submitted.

4. Surface Water Reaction Kinetics

4.1 Research Objectives

The major objective of this project is to evaluate the natural phenomena occurring near the surface of the Berkeley Pit lake, mainly the interaction of UV radiation with the mobile-toxic constituents in the water. Chemical reactions with oxygen coupled to physical processes with UV absorbance in the surface waters of the Berkeley Pit lake seem to be abundant and appear to reduce the concentration of most of the constituents. For example, depth profiles taken on September 5, 1991, by the MBMG show that waters at shallow depths less than approximately 5 meters (surface waters) are significantly warmer, have more DO, are generally less acidic (have higher pH), and have higher E_H levels than those at depths below 25 meters (see Figure 4-1). In fact, the four measured parameters fluctuate in the surface waters and become relatively constant in the deeper waters. Similar profiles have been reported for concentrations of the mobile toxic constituents and are discussed in Section 1. It is believed that UV radiation plays a significant role in the differences between the surface and deep waters. In this regard, experiments on columns of Berkeley Pit lake water collected from the 200-foot level, i.e., deep water samples, were conducted in which the atmosphere and UV wavelength were carefully controlled. Data obtained was expected to provide a basic understanding of the surface waters in terms of how it forms and how fast it is generated. Ultimately, such an understanding could lead to an improved technology for remediating acid-rock drainage systems such as the Berkeley Pit lake.

4.2 Photochemistry

4.2.1 Technology Background

Remediation research of polluted waters originating from active or inactive mines sites and associated materials handling procedures have primarily focused on bringing to the affected areas foreign substances and processes that could ultimately disturb a naturally established ecosystem. Remediation methods by, for example lime addition, are inherently expensive and make the sites difficult to revegetate. Overwhelming evidence shows that natural processes occur that heal environmental scars caused by mining activities. These processes include electron transfer reactions that lower the concentrations of mobile-toxic constituents in the surface and groundwaters through interactions with electromagnetic radiation from the sun, UV light radiation in particular. However, these naturally photoassisted processes suffer at night, on cloudy days, and in winter months. During these periods, artificial UV sources are needed to sustain the process.

In photolysis, solutions are irradiated with electromagnetic radiation, usually UV, to promote electron transfer reactions between species. In acid-rock drainage systems, metal complexes can then either undergo photoreduction or photo-oxidation, depending on the reduction/oxidation (redox) chemistry of the system. The photolytic reaction can be accomplished by direct or indirect methods. Direct photolysis requires the substance being remediated to absorb the radiation. On the other hand, having a second material absorb the radiation and then transfer the photoenergy to the substance being remediated induces indirect photolytic processes. In this regard, absorbing media can be solid semiconductors acting as catalysts (heterogeneous photocatalysis) or can be dissolved in the system either being consumed (homogeneous photolysis) or acting as catalysts as well (homogeneous photocatalysis). Dissolved absorbing media are often referred to as dissolved photosensitizers.

Solid Photocatalysis

To date, most work has focused on studying the

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oxidation of toxic organic compounds using solid semiconductors as electron transfer photocatalysts to ultimately produce both carbon dioxide and water (Refs. 22 and 36-47). However, current emphasis is to apply this technology to inorganic compounds. Various solid photocatalysts have been reported to work with varying degrees of success. The more successful reagents are: titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), cadmium sulfide (CdS), silicon carbide (SiC), ferric oxide (Fe_2O_3), and certain zeolites (Refs. 36-38 and 45). The anatase polymorph of TiO_2 has been favored because it is inexpensive and readily available, and most importantly, it has a high quantum efficiency in converting photon energy into chemical energy (Refs. 48 and 49).

For these solid semiconductors to function as electron photocatalysts, their band gap energies must be less than the absorbed UV radiation as determined from the equation:

$$E = hu \qquad (1)$$

Where h is Planck's constant and u is the frequency of the UV radiation. Upon absorbance, an electron is excited into the conductance band from the valence band where a "hole" is created:

$$\text{Semiconductor} \overset{hu}{Y} (e^- \ h^+) \qquad (2)$$
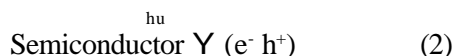
Because the band gap between the conduction and valence band edges lacks energy levels, the excited electron will reside at the conduction band edge, whereas the hole will reside at the valence band edge. Consequently, the electron-hole ($e^-\ h^+$) pair will be relatively stable, possessing a lifetime that is long enough for electron transfer reactions to occur.

$$h^+ + D \ Y \ D^+ \qquad (3)$$

$$e^- + A \ Y \ A^- \qquad (4)$$

This demonstrates that electron donors (D) become oxidized when they release electrons to fill the holes (Reaction 3), and electron acceptors (A) are reduced when they consume the excited electrons (Reaction 4). This photocatalytic process is shown in Figure 4-2.

Solid electron transfer photocatalysis cannot occur unless both A and D are preabsorbed at the semiconductor surface, and the products D^+ and A^- don't react with respective electrons and holes to reproduce the reactants, otherwise no net reaction would result. Furthermore, the Nernst potentials of Reactions 3 and 4 must be thermodynamically favorable. Each of these conditions can be met by: 1) using semiconductors amenable to the adsorption of both A and D but not A^- and D^+, 2) choosing a semiconductor whose band gap is appropriate for the electron transfer reactions to occur, 3) choosing a ligand that reacts with the radical products to form inert species, 4) selecting appropriate pH conditions, 5) stirring/bubbling the system to remove radical products from the surface, 6) depositing metals, i.e., platinum, at the surface as a cocatalyst to localize the excited electrons, and/or 7) promoting reactions between the radical products themselves.

The above discussion demonstrates that the surface reduction/oxidation (redox) and analytical chemistries of solid electron transfer photocatalytic reactions must be well understood before they can be induced and/or enhanced. As stated before, solid photocatalysis has been primarily used to determine the oxidation of toxic organic compounds (Refs. 22 and 36-47). However, the oxidation of inorganic compounds is currently receiving a lot of attention (Refs. 36-39, 43, 45, 50, and 51). However, the results have been less favorable probably due to the fact that reducing power of the excited electron being significantly lower than the oxidizing power of the hole and because the compounds must compete kinetically with oxygen and/or water as the electron acceptor

(Ref. 43).

Dissolved Photolysis

Photochemical reactions in the absence of solid semiconductors have involved both organic and inorganic compounds and have been classified as direct or indirect processes. In indirect photochemical processes, the compound (designated as X in subsequent reactions) absorbs the electomagnetic radiation to form an excited state that reacts to form a variety of products:

$$X + hu \rightarrow X^* \rightarrow products \qquad (5)$$

For most compounds, this reaction is typical of decompositions. For certain inorganic compounds, this reaction either yields changes in oxidation states or transfers the photoenergy to water yielding hydroxyl radicals (OH^*) that can decompose various organic compounds or react with other inorganic species to produce specific radicals (Refs. 22, 52, and 36-39).
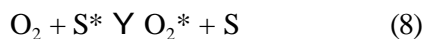
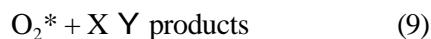With indirect photochemical processes, photosensitizers absorb the radiation:

$$S + hu \rightarrow S^* \qquad (6)$$

and then transfer the photoenergy to the compound, thereby catalyzing the following reaction:

$$S^* + X \rightarrow S + X^* \rightarrow S + products \qquad (7)$$

or transferring the energy to another species (usually oxygen):

$$O_2 + S^* \rightarrow O_2^* + S \qquad (8)$$

to induce the following reaction:

$$O_2^* + X \rightarrow products \qquad (9)$$

Where the O_2^* radical may participate as either a reactant or a cocatalyst. In some cases, the photosensitizer (S) is consumed in the reaction and thus is not considered to be a dissolved photocatalyst.

Each of the radicals mentioned above, i.e., inorganic, organic, hydroxyl, specific photosensitizer, and oxygen, are dissolved and can be induced oxidation (electron donating) or reduction (electron accepting) reactions in the same manner as solid photocatalysts. However, the dissolved photosensitizers (and in some cases dissolved photocatalysts) are not dependent on adsorption and other surface area phenomenon and, by comparison, they can therefore be expected to enhance reaction rates by orders of magnitude. This would only depend on the concentration of the dissolved photosensitizers. Other dissolved photosensitizers include photonactive redox couples where the oxidant would be the electron donor and the reductant would be the electron acceptor.

4.2.2 E_H-pH Diagrams

Because the photolytic processes involve electron transfer reactions, it is helpful to examine thermodynamic equilibrium diagrams such as E_H-pH diagrams to determine what possible reactions may be occurring and what, if any, precipitate might form under these conditions. In this regard, E_H-pH diagrams were generated using STABCAL (Refs. 53 and 54) and have been shown to be reliable in previous and other ongoing MWTP projects (Refs. 55, 56, and 57). STABCAL is a program developed for IBM-compatible personal computers to calculate various types of thermodynamic stability diagrams based on reference data libraries (MINTEQ, NBS, Russian) built into the program.

Thermodynamic Data

The thermodynamic data ($DG_{F298.15}$) used in the construction of E_H-pH diagrams emanates from previous work involving the iron-water system in the Berkeley Pit lake (Ref. 58). These values, in conjunction with the MINTEQ database library,

were used in the construction of the diagrams in this report. Concentrations of metals used in the program were obtained from September 11, 1997, analysis completed for the MWTP. These concentrations are similar, if not the same, as those determined in the research for this report. An ionic strength of 0.4061 was used as determined from the concentrations of all the dissolved constituents.

Figure 4-3 shows an E_H-pH diagram for the iron species at a concentration of 1.91×10^{-2} M, as measured in the Berkeley Pit lake. The point designated by Ú occurs at 0.6 volts (E_H) and 2.65 (pH) and denotes the current conditions in the Berkeley Pit lake at the 200-foot depth, i.e., deep water. The point designated by (occurs at approximately 0.65 volts (E_H) and 2.8 (pH) and denotes the current conditions in the Berkeley Pit lake near the top, i.e., surface water. A comparison to Figure 4-1 shows the current system to be less acidic and more oxidizing than in 1991. Figure 4-3 suggests that the iron should be precipitated as hematite (Fe_2O_3). In this regard, it is important to note that hematite, as mentioned earlier, is a solid photocatalyst and could therefore be a participant in the suspected photolytic behavior of the surface waters of the Berkeley Pit lake system. This explains why valence band holes and conductance band electrons were also illustrated in the plot. Therefore, in accordance with the literature, Figure 4-3. shows hematite with a band gap of 2 volts.

Because the Berkeley Pit lake is a water-based system containing sulfate, schwertmannite [$Fe_8O_8(OH)_6SO_{4E}5H_2O$] would be more likely to precipitate than hematite. In this regard, Figure 4-4 was determined by including 1 M sulfate; the actual sulfate concentration in the Berkeley Pit lake is approximately 0.08 M. This diagram shows schwertmannite being stable where hematite was stable (compare Figure 4-3). Likewise, green rust [$Fe_{4.23}(OH)_{7.88}SO_4$] is shown to be stable where magnetite (Fe_3O_4) was stable. Plotting the same

data points for deep and surface waters shows that no precipitate should form in deep waters, but schwertmannite would be expected to precipitate in surface waters. Furthermore, there is additional reason to suspect that schwertmannite would also behave similarly to hematite and in this regard and should also act like a photocatalyst. Unfortunately, its band gap is unknown and could not be included in Figure 4-4.

Iron Photo-Oxidation
The E_H-pH diagram for the iron-sulfur-water system in Figure 4-4 confirms that iron is present in deep water as ferrous, either as ferrous cation (Fe^{2+}) or as ferrous sulfate ($FeSO_4$). But if conditions are perturbed through UV irradiation, the ferrous cation can be oxidized to ferric cation (Fe^{3+}) by reacting with a hole or perhaps a hydroxide radical, either of which can be produced at the surface of a photocatalyst (possibly schwertmannite) on UV absorbance.

$$Fe^{2+} + h^+ \text{ Y } Fe^{3+} \qquad (10a)$$

$$Fe^{2+} + OH^* \text{ Y } Fe^{3+} + OH^- \qquad (10b)$$
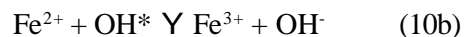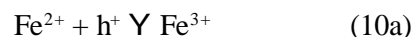
Ferrous cations can also be oxidized to ferric cations by dissolved photosensitizers. Upon UV absorbance, the photosensitizers become radicals and act as electron acceptors or scavengers.

$$Fe^{2+} + A^* \text{ Y } Fe^{3+} + A^- \qquad (11)$$
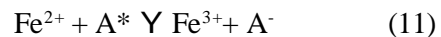
This latter reaction can also involve hydroxyl radicals but is distinguished from the photocatalytic reaction because it is a bulk reaction independent of surface phenomena. It is interesting that Reaction 10b indicates both the oxidation potential and the pH should increase, which concurs with the information given in Figures 4-1, 4-3 and 4-4. Because ferric cations are relatively unstable in water at these pH and E_H conditions, an immediate reaction with water, DO, and/or sulfate will occur precipitating hematite, schwertmannite, and/or

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other similar iron species, such as ferrihydrite [Fe(OH)$_3$].

Other Mobile Toxic Constituents

Other mobile toxic constituents could behave in this manner. Arsenic, for example, is known to respond well to photolysis. In the case of the Berkeley Pit lake water, it is photo-oxidized to arsenate (see Figure 4-5) and removed from solution by adsorption at the surface of any of the iron precipitates that may form as just noted. In

this regard, it is important to note that the BDAT for removing arsenic from wastewaters is by oxidizing the arsenic and then adsorbing it at the surface of precipitated ferrihydrite.

4.3 Treatability

4.3.1 General Test Procedures

For this project, experiments were conducted in a column measuring 12-feet high with a 6-inch inner diameter (ID). The column was made of UV-resistant Schedule 40 (polyvinyl chloride) PVC and located in the High Bay of the Engineering and Laboratory Classroom (ELC) Building at Montana Tech. At the top of the column, a PVC box was placed to house the UV sources with rated intensities of 600 microwatts per square centimeter and either 254 nm or 365 nm wavelengths UV radiation. A specific atmosphere of either air or nitrogen was maintained in the box immediately above the surface of the water in the column (see Table 4-1). Because the atmosphere was continuously supplied from pressurized gas cylinders, heat produced from the UV sources was continuously removed, thereby helping to control the temperature of the atmosphere. It was initially discovered that over a period of 3 weeks, between 6 inches and 1 foot of water was lost due to evaporation. Because this was attributed to the purge gas being dry, the purge gas was blown through a bubbler before entering the box. This prevented the loss of water and also helped to visually control the flow rate of purge gas being

used.

Using 1/2-inch-ID PVC pipe attached to the bottom of the column, the column was gently filled from the bottom with 17 gallons of deep Berkeley Pit lake water collected and transported by the MBMG. The remaining 8 gallons were stored in a refrigerator at 4 EC to help maintain freshness for future use to keep the level in the column constant. Because the 1/2-inch pipe allowed fresh water to be introduced into the bottom of the column, no disturbances to the water at the top of the column should have been realized.

4.3.2 Sampling and Calibration

Valved sample ports were placed 6 inches apart through the length of the column to collect samples for measuring concentrations as a function of height at the conclusion of each test, usually after 3 weeks. The 25-mL sampling vials were used to collect the samples. All samples were acidified to a pH<2 to preserve them for future analysis. Until they were analyzed, the samples were stored in the refrigerator at 4 EC. Eventually all samples were sent to Rocky Mountain Labs for analysis.

At weekly intervals, a Data Sonde Multiprobe Logger or Hydrolab were used to measure pH, DO, E$_H$, temperature, conductivity, and turbidity as a function of depth. Because the physical dimensions of the Hydrolab (3 inches ID and 15 inches long) were fairly large, it was lowered slowly with a manual pulley system to minimize disturbances due to the significant displacement of water. Typically, 25 positions approximately 6 inches apart in the column were measured with each position taking approximately 10 minutes to measure. In this regard, over 4 hours would elapse before all measurements were completed. However, it is important to note that the Hydrolab had to be withdrawn from the column equally slowly meaning that as much as 8 hours was used to complete the weekly measurements. A microcomputer inside the Hydrolab stored the information that was downloaded to a personal

computer at the conclusion of each weekly measurement.

Before each weekly measurement, the Hydrolab was calibrated according to the manufacturer's specifications and always in accordance with quality assurance/quality control (QA/QC) protocol. Following downloading, the data, which consisted of three values, was averaged and imported into a spreadsheet. Graphs of the averages were then constructed and compared with other weekly test measurements as well as with the same week of other tests.

4.3.3 Experimental Results

It will be indicated that the results show distinct profiles being developed over the 3-week periods, although none look as satisfactory as those shown earlier in Figure 4-1. For each experiment, equilibrium appears to have been achieved during the third week. As noted earlier, analyses are made by dynamically examining the changes as a function of time and by statically comparing the tests at equivalent times. Results are presented in Figures 4-6 to 4-22. The ensuing discussions will help determine the effects of UV radiation and atmospheric conditions on surface waters.

Background Experiment

Once all experimental details and nuances were determined, the background experiment was conducted. This experiment, as noted earlier in Table 4-1, did not employ UV radiation or a continually supplied gas to control the atmosphere. The experiment was stagnant and therefore was simply allowed to sit for 3 weeks while Hydrolab measurements were taken weekly and samples for solution analysis were taken at the conclusion. Results are presented in Figures 4-6 to 4-13. This information, once presented, is the focal point of the ensuing discussions since it is to be compared to the results obtained in the other experiments when the UV and gas parameters were systematically changed. Differences between this

experiment and the tests will be attributable to the process.

Temperature: When the Berkeley Pit lake water was introduced into the column, it was shown to have a temperature of 11 EC. Temperature profiles were then recorded weekly. Results in Figure 4-6 show the water gradually warmed with time to nearly 24 EC in the third week. However, each of the profiles illustrate the surface water is nearly 1 degree warmer than the deepest water after a week. Even though the temperatures increased weekly, the profiles are relatively constant. In this regard, it is not expected that major differences in the other variables will be observed. It is important to note that these temperatures are close enough to 25 EC, which was assumed for the thermodynamic calculations used to depict the E_H-pH diagrams discussed earlier and presented later, that their use will acceptable.

pH: The pH of the Berkeley Pit lake water introduced into the column measured 2.71. Subsequent pH profiles show the water gradually becoming more acidic, eventually yielding a near constant pH of 2.63 in week 3 (see Figure 4-7). This behavior can be explained by the consumption of hydroxide by ferric cations and hence their precipitation as schwertmannite or ferrihydrite. To illustrate, ferrihydrite precipitation is given by:

$$Fe^{3+} + 3OH^- \quad Y \quad Fe(OH)_3 \qquad (12)$$
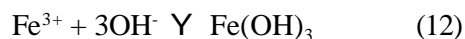
However, because the Berkeley Pit lake water being used is deep water, most of the iron present should originally be ferrous meaning that the ferric cations discussed above had to be generated. The most likely reaction for this is:

$$Fe^{2+} + \frac{1}{2}H_2O + \frac{1}{4}O_2 \quad Y \quad Fe^{3+} + OH^- \qquad (13)$$
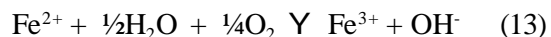
where the oxygen is present as dissolved oxygen.

This helps explain why there was an initial pH

increase in the system from pH 2.71 to 2.80. Overall, 2 M of hydroxide must be consumed for every mole of iron precipitated, thereby explaining the continual decrease in pH. Each of the profiles clearly show that the pH is greatest near the surface and decreases to some constant value with depth. In this regard, no major difference was found in the pH profiles.

Dissolved Oxygen: Because the initial DO concentration in the Berkeley Pit lake water introduced into the column was found to be 1.2 ppm, the increased DO near the surface water can be attributed to adsorption from the atmosphere and/or diffusion/mass transfer from the depths below (see Figure 4-8). Eventually, according to the pH discussion above, DO concentrations should be consumed. This clearly appears to be the case.

Turbidity: Initially, the Berkeley Pit lake water contained no turbidity. However, Figure 4-9 shows turbidity forming within the first week. This is obviously caused by the precipitation of the iron as discussed above. The profiles in Figure 4-9 suggest the precipitates settle by week 2 since very little turbidity remains by that time. In fact, at the conclusion of the test, a considerable amount of sludge was found at the bottom of the column.

Specific Conductivity: Figure 4-10 shows the effect of depth on the SC of the Berkeley Pit lake water as a function of time. Results show that the surface zone is less conductive than the depth, a difference that is most pronounced early on when the precipitation process is underway. However, as the precipitates settle and presumably form in lesser amounts, the column system appears to approach a constant value near 8,400 microseconds per centimeter (Fs/cm). This is an indication that, after 3 weeks, the column is well mixed and therefore is indeed close to equilibrium. This suggests that running the experiments for 3 weeks was an appropriate decision.

Redox Potential (E_H): The Berkeley Pit lake introduced to the column had an E_H measuring 650 mV. After a week, Figure 4-11 shows that E_H slightly increased to approximately 652 mV in the surface and to a slightly more oxidizing potential of 655 mV at depth. This appears to confirm that ferrous-to-ferric oxidation may be occurring. In the subsequent weeks, this scenario was reversed and more oxidizing potentials near 659 mV were found in the surface water and more reducing potentials near 648 mV were observed at depth. The significance of these measurements is best realized when the E_H and pH values are compared. In this regard, it is noted that as the pH decreases, the E_H increases. Plotting the data on an E_H-pH diagram further shows that the E_H and pH may be controlled by a chemical reaction, presumably ferrous cations oxidizing to ferric cations and eventually precipitating as schwertmannite (see Figure 4-12).

Metal Concentrations: Figure 4-13 shows that the final concentrations of iron, zinc, aluminum, and copper are fairly constant through the length of the column. Only iron levels appear to increase with increasing depth, which is probably the result of iron precipitates redissolving under the slightly reducing conditions that exist at depth. By comparison to its initial concentration, iron decreased from 1,200 ppm to approximately 950 ppm, clearly indicating that iron was indeed precipitating. The other metal concentrations also decreased; however, the change was minimal and probably due solely to adsorption at the surface of the iron precipitates as opposed to a separate precipitation event. In this regard, zinc, aluminum, and copper concentrations decreased from approximately 590, 290, and 190 ppm to approximately 570, 280, and 165 ppm, respectively. These final concentrations were nearly constant throughout the length of the column.

UV-Irradiated Tests
When a column of Berkeley Pit lake water is exposed to UV radiation and a continual flow of a gas, differences from the background experiment

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can be attributed to the evaporation process. However, the wealth of data accumulated with these tests makes it virtually impossible to plot everything. In this regard, the number of plots is minimized such that only significant differences between these tests and the background experiment are discussed. However, general trends are mentioned briefly.

Temperature: Temperature profiles reveal that, as time progresses, the column of Berkeley Pit lake water slowly warms to the room temperature of the High Bay where the tests were conducted. In this regard, absolute temperature changes were minimal and approximately the same as those presented earlier in Figure 4-6 for the background experiment.

pH: As with the temperature profiles, the pH profiles were similar to the background experiment such that the pH was observed to decrease with time and the pH at the surface was higher than it was at depth. However, unlike the background experiment, the initial increase in the pH was lessened. A typical profile is shown in Figure 4-14 to illustrate this behavior. This can be attributed to photolytic reactions and includes reacting with valence band holes possibly from a schwertmannite precipitate (Reaction 10a) or an electron-accepting photosensitizer (Reaction 11). Obviously, for Reaction 10a to occur on schwertmannite, the precipitate must have already formed by Reaction 12 through either Reaction 10b or 13. This would not be the case in the column work but would be in the Berkeley Pit lake itself. Likewise, Reaction 10b could be induced by, for example, hydroxyl or organic radicals. The presence of organic compounds in the Berkeley Pit lake waters is only now being documented but appears to be a possible cause. Clearly, Reactions 10a and 11 do not yield hydroxide species like that shown in Reaction 13. In this case, the precipitation of ferrihydrite (Reaction 12) would still occur but would consume three hydroxides for every ferric cation consumed (as opposed to two). In this regard, the pH values should be lower for the UV-irradiated tests than the background experiment. A comparison of Figures 4-7 and 4-14 confirms this hypothesis.

Dissolved Oxygen: If Reaction 13 is minimized because most of the ferrous is being photolytically converted to ferric instead of chemically, DO consumption should be minimal, and therefore DO concentrations should be significantly higher in the UV-irradiated tests than in the background experiment. Figure 4-15 shows the DO profiles for each test in the third week. A comparison to Figure 4-8 confirms that DO consumption is minimal even when a nitrogen gas purge was used. Further comparison shows that the profiles exhibit the same general trend as discussed for the background experiment: DO concentrations are highest in the surface and lowest at depth where they converge near 0.4 ppm.

Turbidity: Differences in turbidity appear to be minimal. All tests yielded relatively high turbidity in the first week; however, subsequent settling allowed the turbidity to decrease significantly by the third week. Differences that do exist could be attributed to the size of the precipitates. The larger the precipitates, the faster their settling rates would be, and hence the less the turbidity would be. In this regard, it was noted that three of the four UV- irradiated tests in weeks 2 and 3 gave turbidity numbers higher than the background experiment. This suggests that UV irradiation may cause smaller particles to precipitate. However, because there was no overwhelming evidence to say otherwise, no correlation could be ascertained as to the conditions, i.e., UV-irradiated or nitrogen-exposed, needed to produce smaller precipitates. Furthermore, particle size analysis was not conducted as part of this study.

Specific Conductivity: The UV-irradiated tests yielded SC profiles that showed a sharp increase from the surface to a shallow depth near the 1.5-

foot level after which, and for the most part, it plateaued to a constant value between 8,000 and 8,500 Ƒs/cm. This is shown in Figure 4-16 for week 3 data, which clearly suggests the column experiments were perfectly mixed except for the first 1.5 feet. For the most part, this slightly contrasts with the background experiment because the transition to a constant value was gradual and was not observed until the 5-foot level was reached (compare Figure 4-9).

Redox Potential: Figure 4-17 shows how E_H typically changes with depth for the UV-irradiated tests. In the deeper waters, the E_H was observed to decrease independent of UV irradiation. However, it is surprising to note that the E_H in the shallow waters decreased with time in contrast with observations for the background experiment (compare Figure 4-11). Surprisingly, the effect is observed when air in the purging gas, i.e., oxygen gas, is present. Furthermore, the effect is more pronounced when either nitrogen or 254-nm UV radiation is used. Clearly, the UV radiation is influencing the chemistry in the surface waters; however, it cannot be ascertained if this effect is caused by a dissolved photosensitizer or a solid photocatalyst (see Reactions 10 a and 11). The dissolved photosensitizer could be an organic in the Berkeley Pit lake water as well as the ferric cations that are produced on ferrous oxidation (Reactions 10a, 10b, and 13). Figure 4-18 shows UV-vis spectra of iron(III), iron(II), copper(II), and zinc(II) sulfate dissolved in water at concentrations equivalent to the metal species in Berkeley Pit lake water. The spectra are compared to those obtained from the Berkeley Pit lake water as well as a Berkeley Pit lake precipitate that was filtered, dried, and repulped. It is worth noting that the Berkeley Pit lake water, iron (III) sulfate solution and precipitate (most likely schwertmannite) are strong UV absorbents, particularly at the 254-nm and 365-nm UV radiation used in this study. Recall that being a UV absorbent is a precursor to being a photolytic reagent.

Finally, it can be noted that the E_H values determined in the UV-irradiated tests (653 to 658 mV) are nearly the same as those found in the background experiment (647 to 659 mV). Because the measured pH ranges are nearly the same as well, i.e., 2.60 to 2.78 vs. 2.63 to 2.80, the data would plot on an E_H-pH diagram in much the same manner as the background experiment (see Figure 4-12). Clearly, schwertmannite precipitation would not be prevented (at least at the UV intensity used). However, it is interesting to note that the lower E_H realized with UV irradiation could have slowed down the precipitation rate that could, in turn, have prevented larger precipitates from forming. The formation of smaller precipitates with UV irradiation was inferred from the turbidity discussion above.

Metal Concentrations: Similar to the background experiment, the final concentrations of iron, zinc, aluminum, and copper are fairly constant through the length of the column (see Figures 4-18 to 4-22). No matter what the conditions were, iron consistently increased with increasing depth and yielded approximately the same final concentration as before, i.e., 950 ppm. This is critical to know because it suggests the UV-irradiated tests and the background experiment oxidized the same amount of iron which, in turn, suggests that there are two different reactions at work. The first is the electrochemical reaction (Reaction 13) and the second is the photochemical reaction (Reaction 10a, 10b, or 11), both of which oxidize ferrous to ferric.

Likewise, the other metal concentrations also decreased, but the change was minimal. However, the conditions did seem to have a considerable influence on their final concentrations. Both zinc and aluminum concentration profiles remained constant at respective concentrations of 570 and 280 ppm through the length of the column when nitrogen was being used as the purge gas. These

concentrations are the same as obtained in the background experiment. However, when air was the purge gas, zinc and aluminum concentrations were found to increase with depth, yielding concentrations at the bottom of the column above the initial concentration of the Berkeley Pit lake water. In this regard, zinc and aluminum concentrations increased from approximately 590 and 290 ppm to approximately 610 and 300 ppm, respectively. This is an indication that the zinc and aluminum are precipitating with the schwertmannite and redissolving at depth. It is unlikely that such an event is due to adsorption/desorption phenomena considering the surface conditions on the precipitate will not change greatly under conditions in the surface waters compared to deeper waters.

On the other hand, copper concentrations were also found to slightly increase with increasing depth but were independent of the purging gas being used. In this case, copper concentrations increased from 175 ppm at the surface to just over 180 ppm at

depth. These concentrations are only slightly below the initial concentration of 190 ppm but are higher than the 165 ppm observed for the background experiment. It is interesting that UV irradiation helps keep the copper in solution. This behavior was observed before using experiments in beakers but is surprising to be observed in much larger and deeper columns, considering that UV radiation only penetrates into water a few centimeters at best. In this regard, it is suspected that a chain reaction is occurring. To visualize this, a series of molecules are linked together through Van der Waals forces or some other weak bond. These chains exist throughout the column and can be depicted by a series of Xs:

$$X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X \quad (14)$$
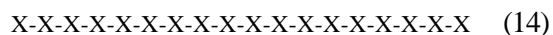
If UV radiation is absorbed by the first X, which is at the top of the column, then it will become

excited and form X* in the same manner that a photosensitizer becomes a radical:

$$X^*-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X \quad (15)$$
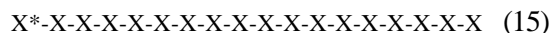
Because of the bonding between the Xs, photoenergy can be transferred down the chain to any X in the chain and therefore anywhere in the column. For the terminal X, the following would be depicted:

$$X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X-X^* \quad (16)$$
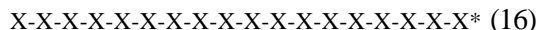
For this to occur, X must be present and in significant amounts. Because anything at low concentration can be eliminated from consideration, the iron, sulfate, and organic compounds in the Berkeley Pit lake water may exist in sufficient quantities for this purpose. The UV spectra shown earlier in Figure 4-18 concur with this possibility. This suggests that the photochemical reactions in the column, and therefore in the Berkeley Pit lake itself, are predominantly induced by dissolved photosensitizers. Reaction 11, therefore, should dominate the system. Furthermore, because the photoenergy can be delivered to any position in the column, it would be reasonable to conclude that the column should be nearly well mixed in regard to dissolved species, i.e., not the solids, which are allowed to settle out of the quiescent waters. The constant SC profiles measured in the presence of UV radiation seem to verify this behavior. Such profiles were nonexistent in the absence of UV radiation.
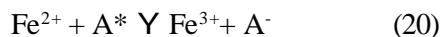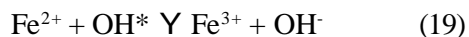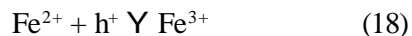
4.3.4 Summary
The experimental data demonstrates that UV radiation has an effect on the surface waters of the Berkeley Pit lake. Depth profiles for most of the measured parameters (temperature, pH, DO, turbidity, SC, E_H, and the concentration of metals including iron, zinc, aluminum, and copper) were found to be significantly different from those determined for the background experiment in the

absence of UV radiation. Profiles for pH helped show that two reactions are at work. The first is the ferrous-to-ferric oxidation reaction which, in the absence of UV radiation is:

$$Fe^{2+} + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \; Y \; Fe^{3+} + OH^- \quad (17)$$
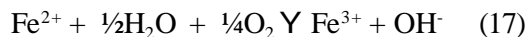
This reaction was confirmed when it was found pH values increased and DO concentrations decreased but not as appreciably as when UV irradiation was employed. Consequently, it was concluded that ferric formation had to occur through another mechanism in the presence of UV radiation. In this regard, the second reaction involves one and possibly all of the following:

$$Fe^{2+} + h^+ \; Y \; Fe^{3+} \quad (18)$$

$$Fe^{2+} + OH^* \; Y \; Fe^{3+} + OH^- \quad (19)$$

$$Fe^{2+} + A^* \; Y \; Fe^{3+} + A^- \quad (20)$$

The first two reactions (18 and 19) involve solid photocatalysts, whereas the third (20) involves dissolved photosensitizers. Not enough data was ascertained to determine which of these photoreactions was occurring. However, a chain reaction mechanism was proposed to account for the SC profiles observed with UV irradiation.

This further suggested that it was dissolved photosensitizers involved, and hence it was Reaction 20 that dominated the process. This is not to say that the first two reactions do not occur.

Finally, it was also concluded that schwertmannite was being precipitated since points plotted on E_H-pH diagrams were consistently on the equilibrium line between schwertmannite and two dissolved ferrous species: ferrous cation and ferrous sulfate. Because it is suspected that schwertmannite will behave like hematite, photocatalysis may play a significant role in the Berkeley Pit lake. Waves in the system will help keep the surface waters stirred, thereby keeping the schwertmannite precipitate near the surface where UV radiation is present. However, the effect of schwertmannite is minimal in the column experiments because they were conducted such that no schwertmannite was initially present and because the quiescent conditions allowed it to settle out. In this regard, it appears that dissolved photolysis with photosensitizers is dominant but may not be the only UV mechanism involved in the column research. Consequently, it is concluded that photolytic processes may be used to influence the chemistry of the Berkeley Pit lake water. Future investigations should continue to see if these processes can be enhanced to improve them and thereby develop new and perhaps better remediation technologies.
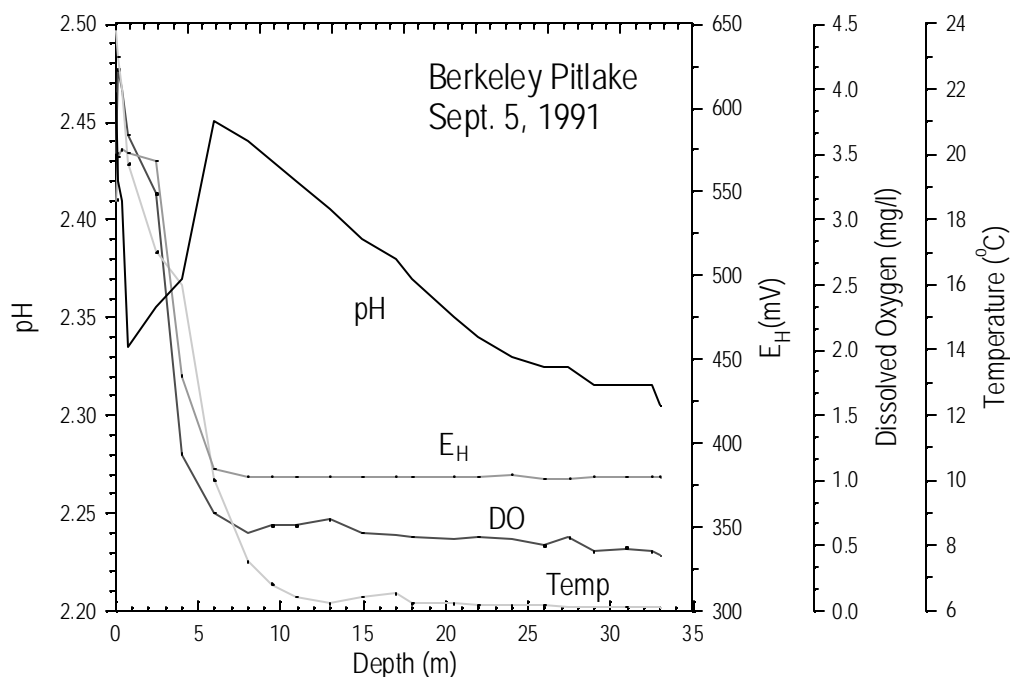
Figure 4-1. Depth profiles of pH, E_H, DO, and temperature determined by MBMG on September 5, 1991, for the Berkeley Pit lake.
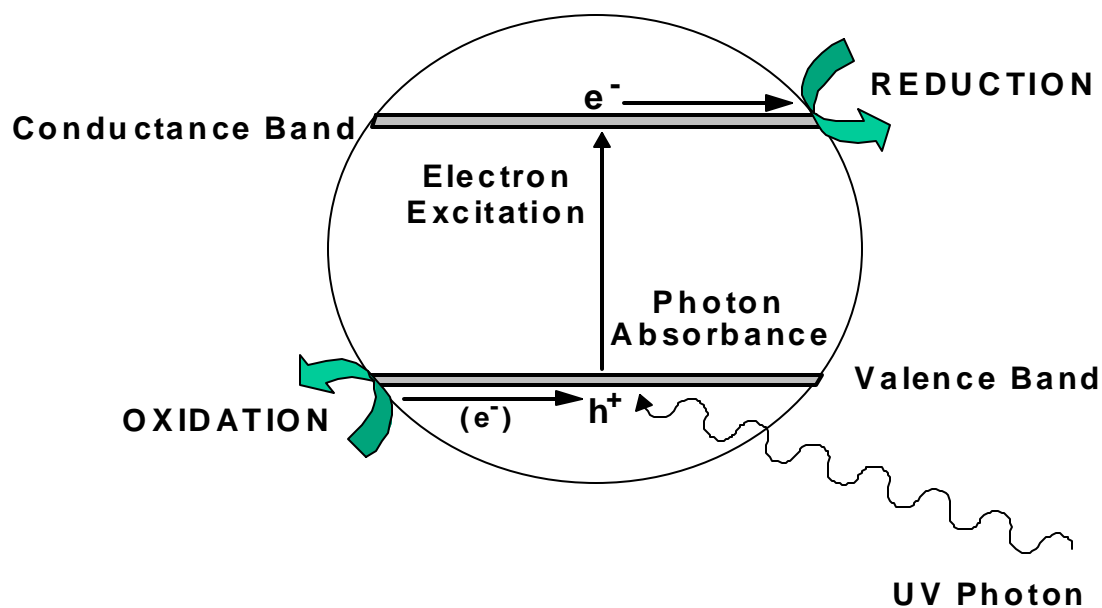

Figure 4-2. Photocatalytic process illustrating the formation of holes (h+) in the valence band and excited electrons (e-) in the conductance band on absorbance of photons with energies greater than the band gap and typically with UV frequencies.
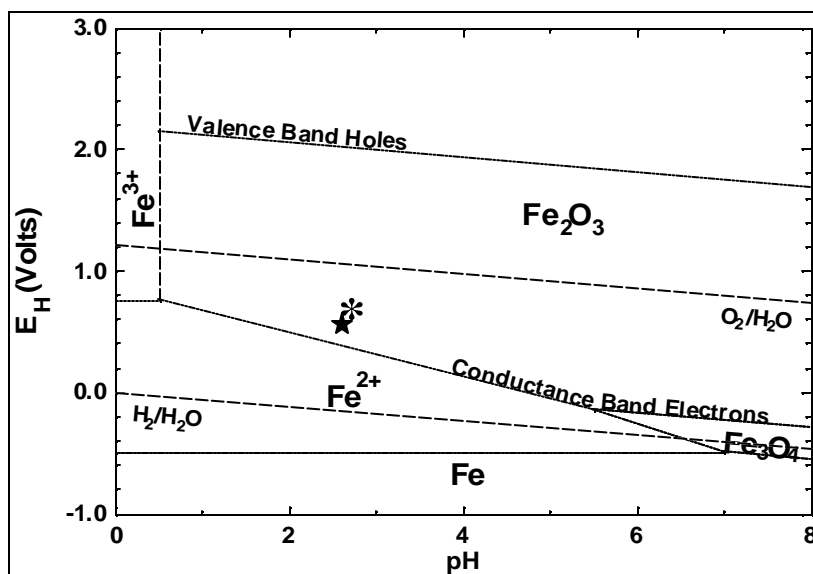
Figure 4-3. E_H-pH diagram for the iron-water system at a concentration of 1.91×10^{-2} M. The water stability region is shown with dashed lines. Points designated with Ú and (denote the current conditions in the Berkeley Pit lake in the deep and surface waters, respectively.
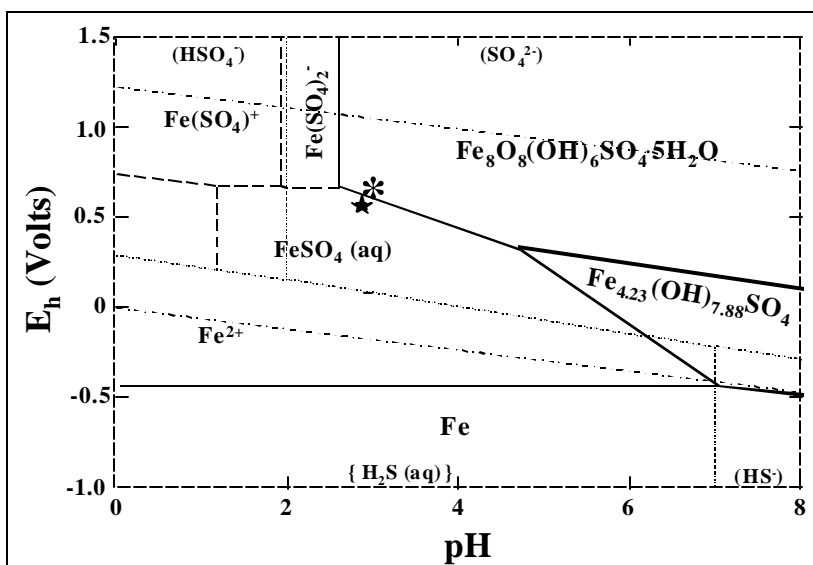

Figure 4-4. E_H-pH diagram for the iron-sulfur-water system with an iron concentration of 1.91×10^{-2} M and a sulfur concentration of 0.1 M. The water stability region is shown with dashed lines. Points designated with Ú and (denote the current conditions in the Berkeley Pit lake in the deep and surface waters, respectively.

Figure 4-5. E$_H$-pH diagram for the arsenic-sulfur-water system with an arsenic concentration of 1x10^{-4} M and a sulfur concentration of 0.1 M. The water stability region is shown with dashed lines. Points designated with Ú and (denote the current conditions in the Berkeley Pit lake in the deep and surface waters, respectively.
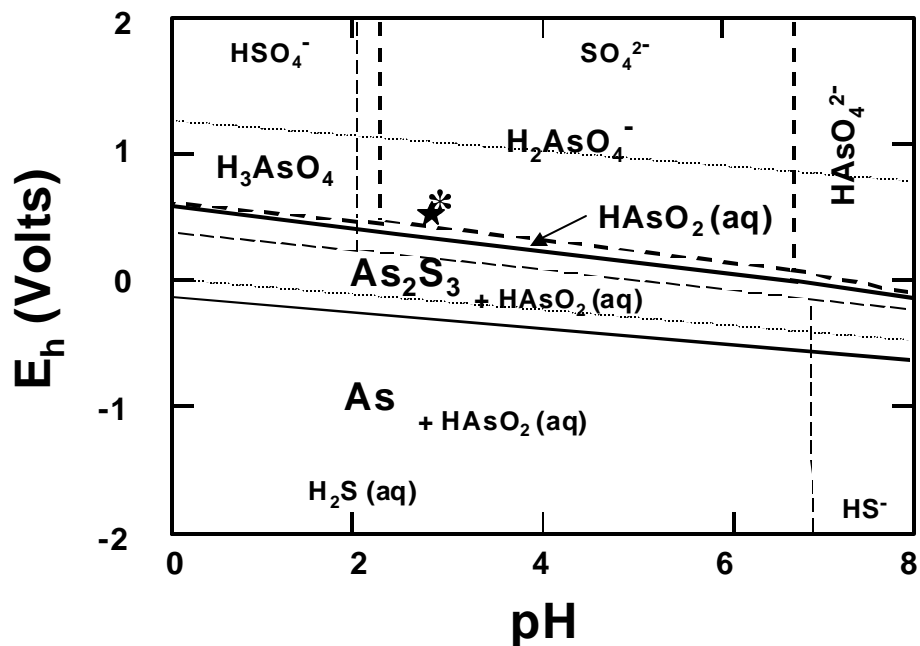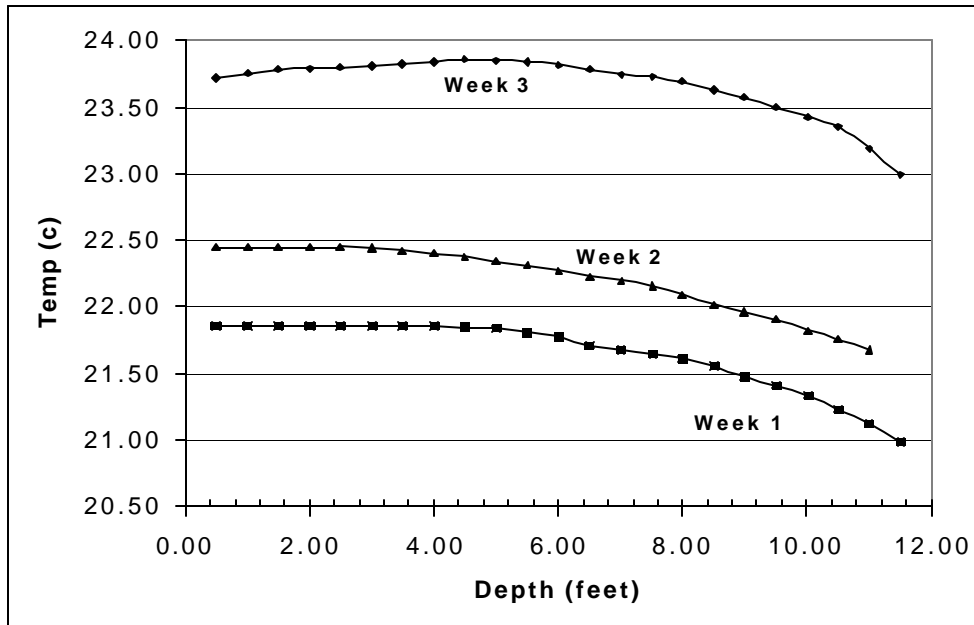

Figure 4-6. Temperature (EC) as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.
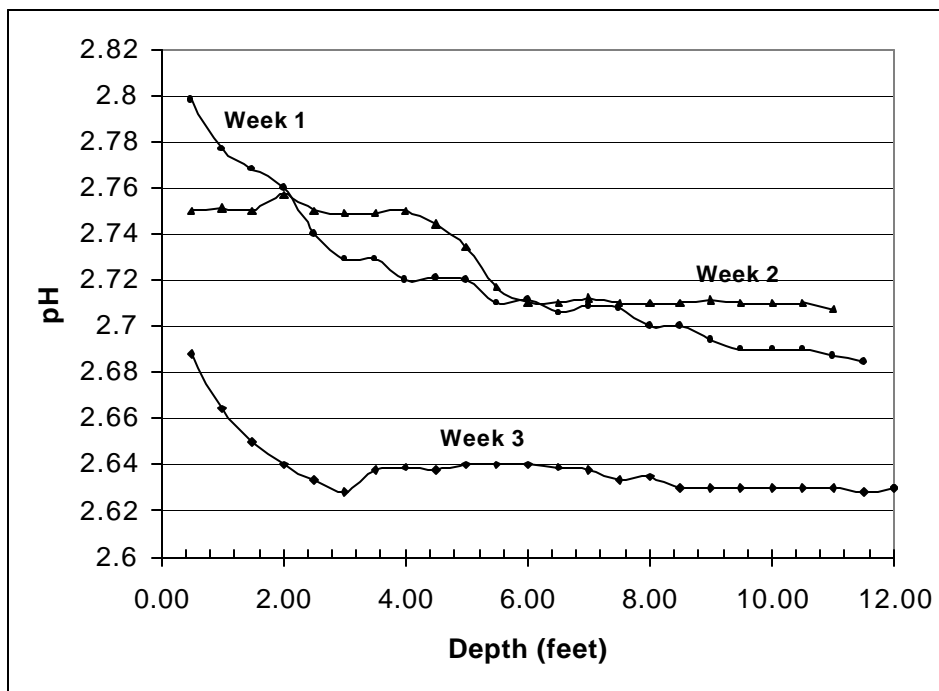
Figure 4-7. pH as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.

Figure 4-8. Dissolved oxygen (ppm) as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.

Figure 4-9. Turbidity (ntu) as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.

Figure 4-10. Specific Conductivity (Fs/cm) as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.
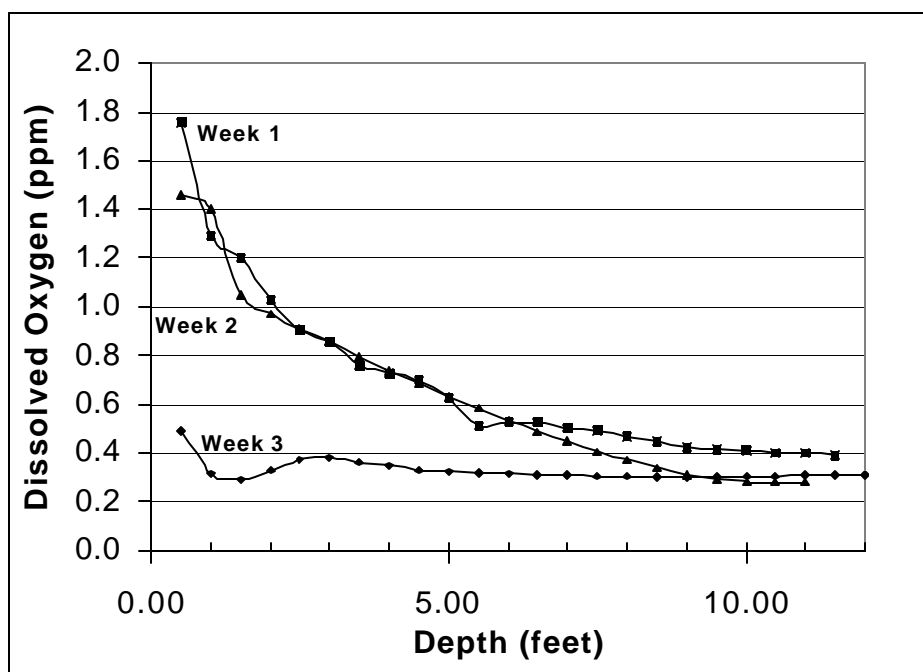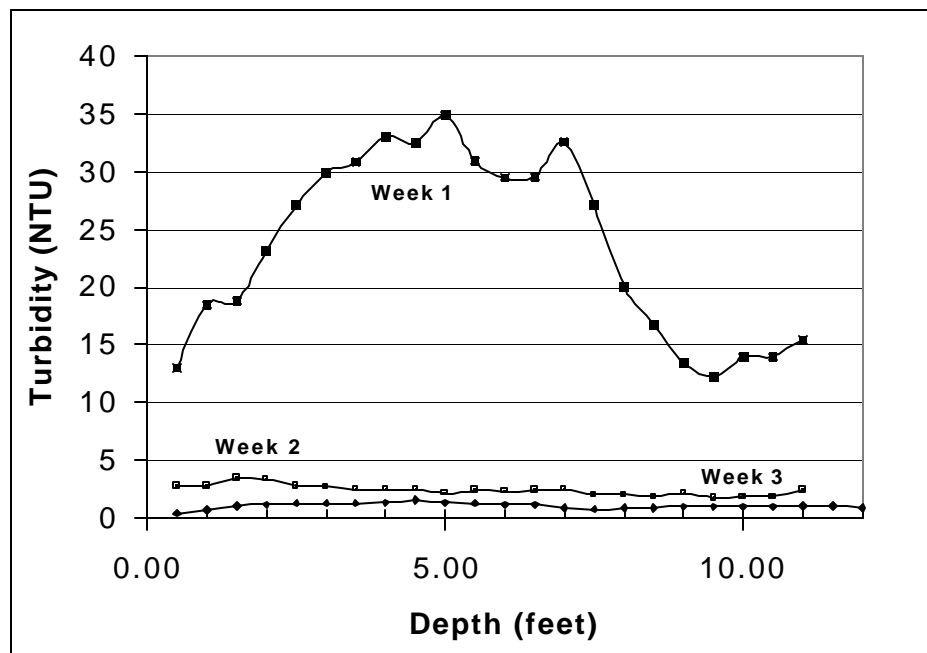
Figure 4-11. Redox potential as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.
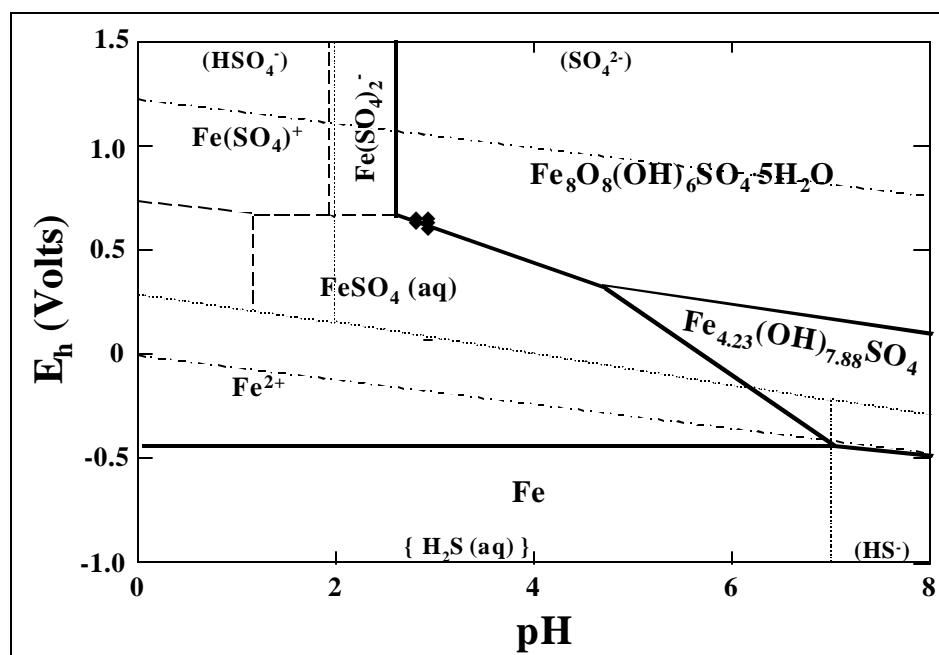
Figure 4-12. Redox potential-pH diagram for iron-sulfur-water system using concentrations equivalent to Berkeley Pit lake water (1.91×10^{-2} M iron and 1.0 M sulfur). Data points near 0.65 volts and pH 2.7 were measured over a 3-week period as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water.

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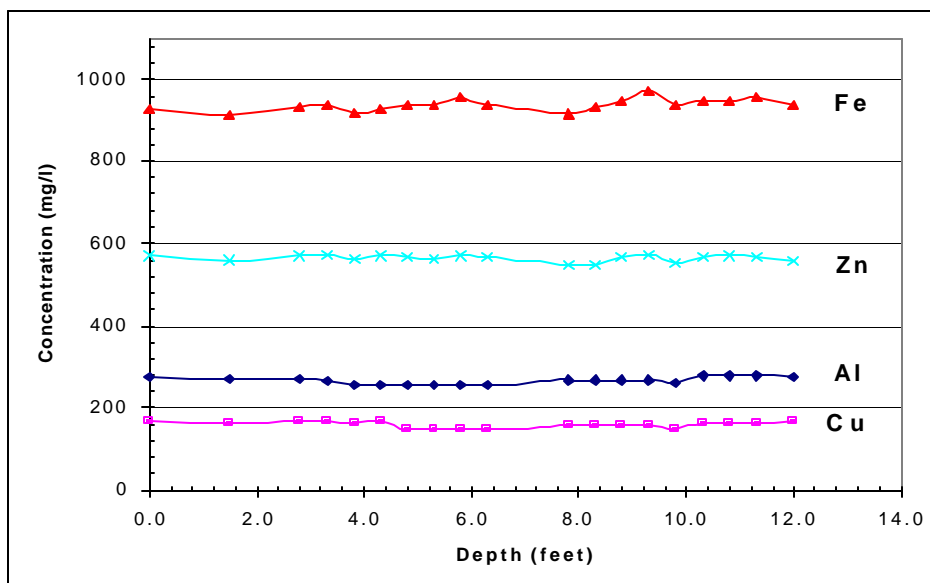
Figure 4-13. Iron, zinc, aluminum, and copper concentrations as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.
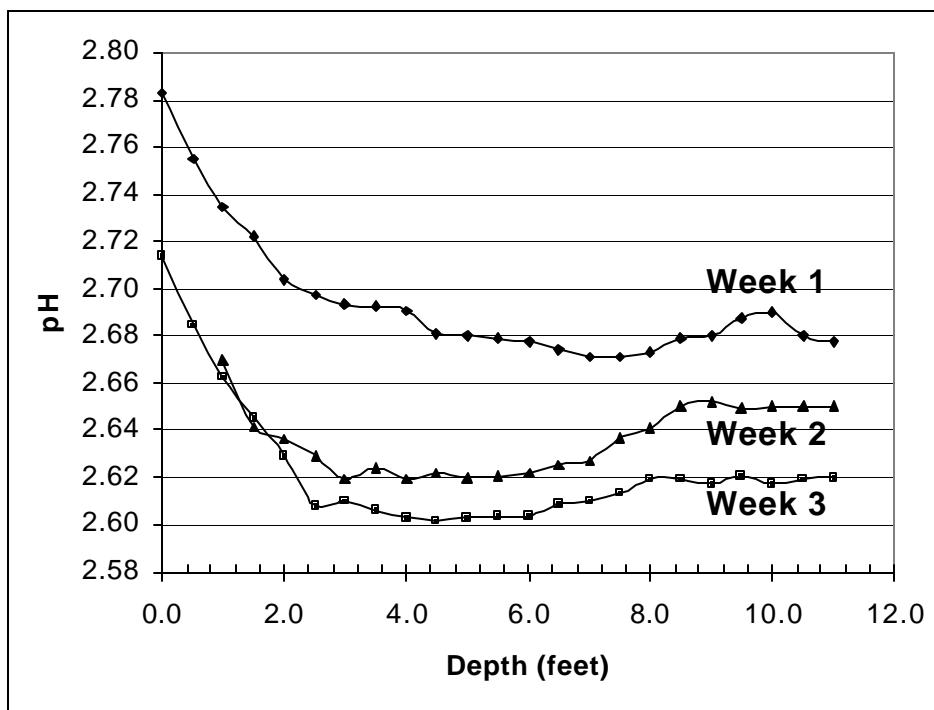
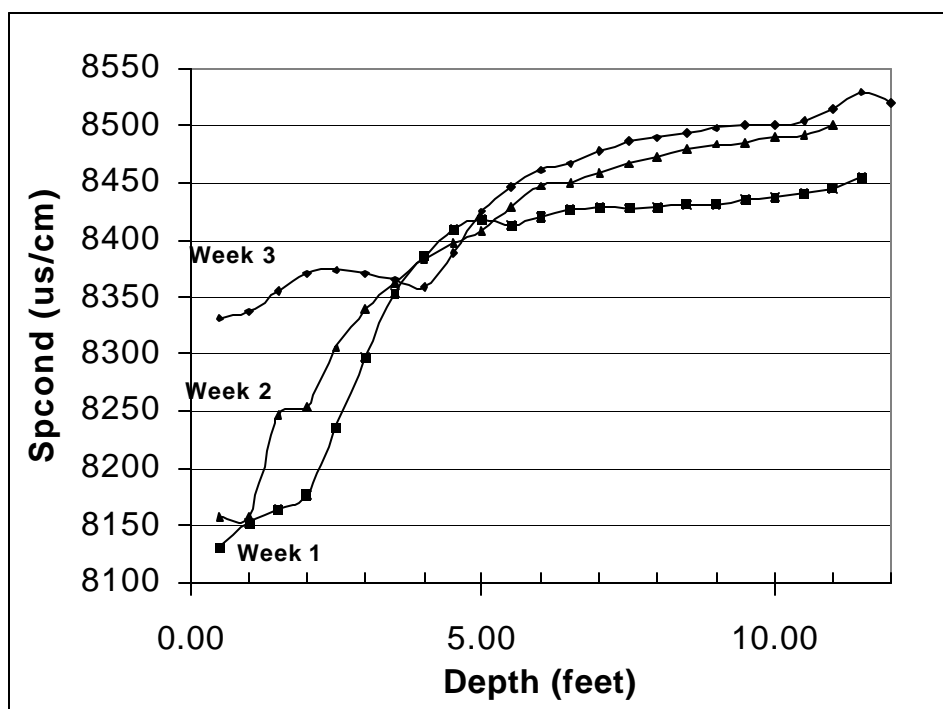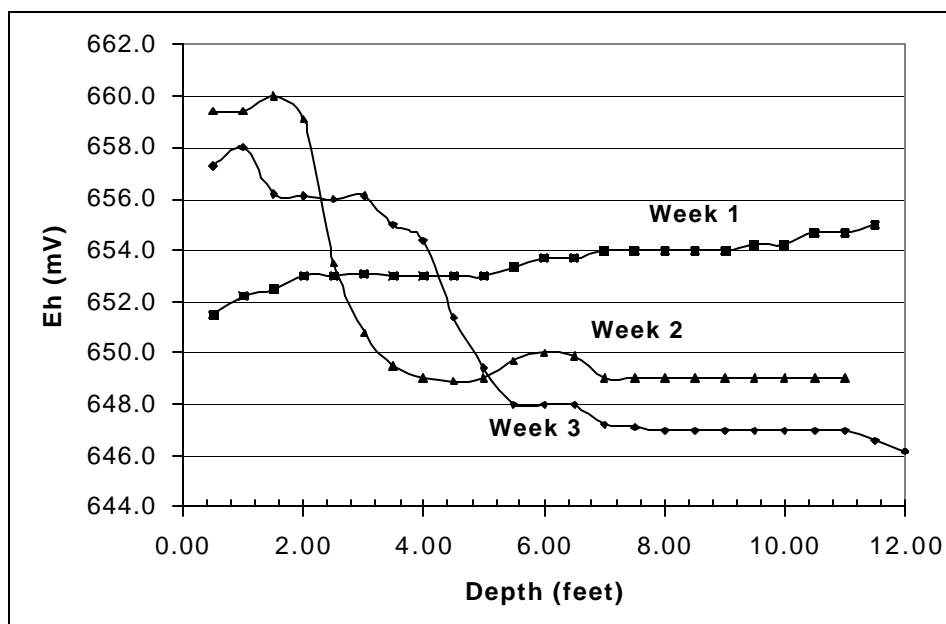**Figure 4-14. Typical effect of UV irradiation and atmospheric control on pH as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.**
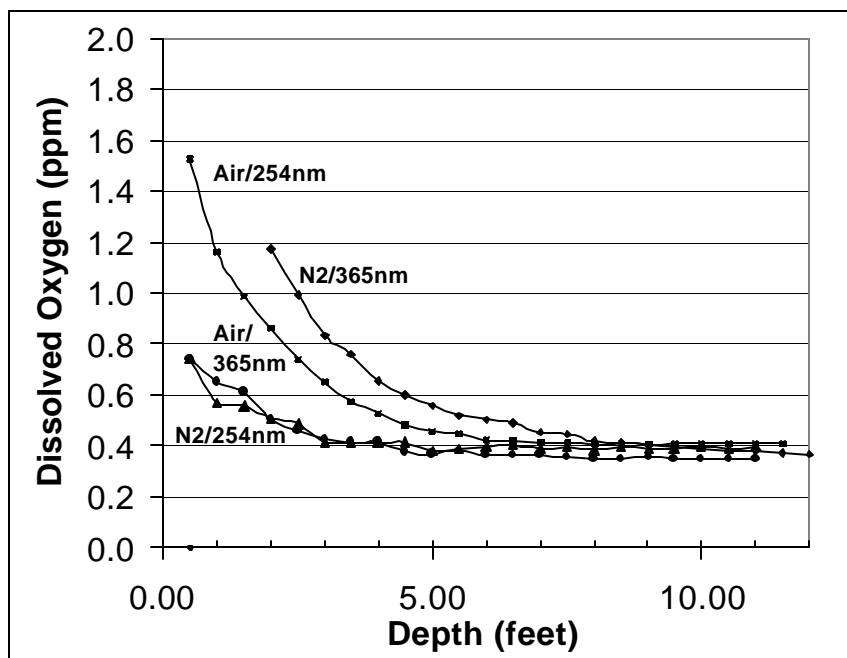
Figure 4-15. Effect of UV irradiation and atmospheric control on DO as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured during Week 3.
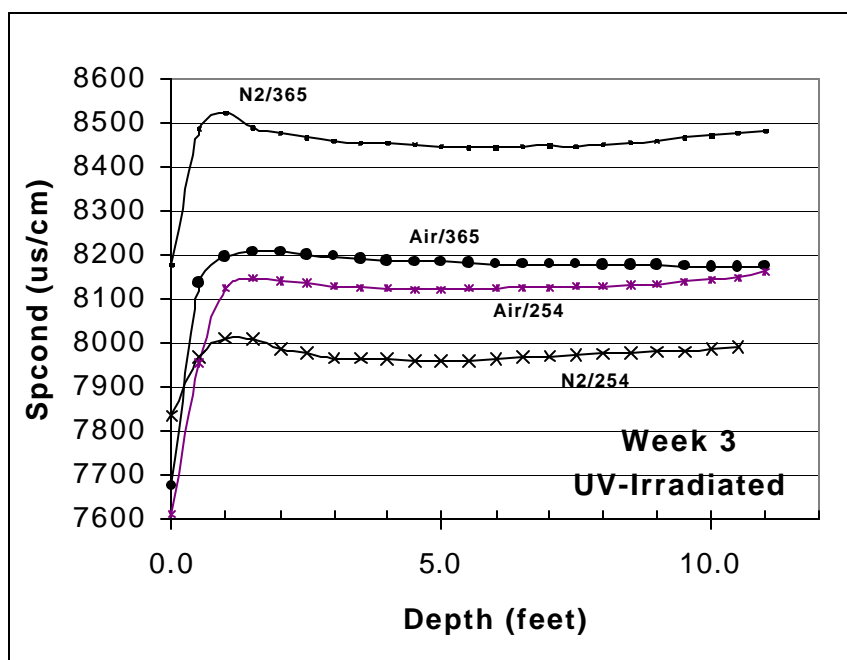
Figure 4-16. Effect of UV irradiation and atmospheric control on Specific Conductivity as a function of depth (ft) in a 6-inch column of Berkeley Pit lake water as measured during Week 3.
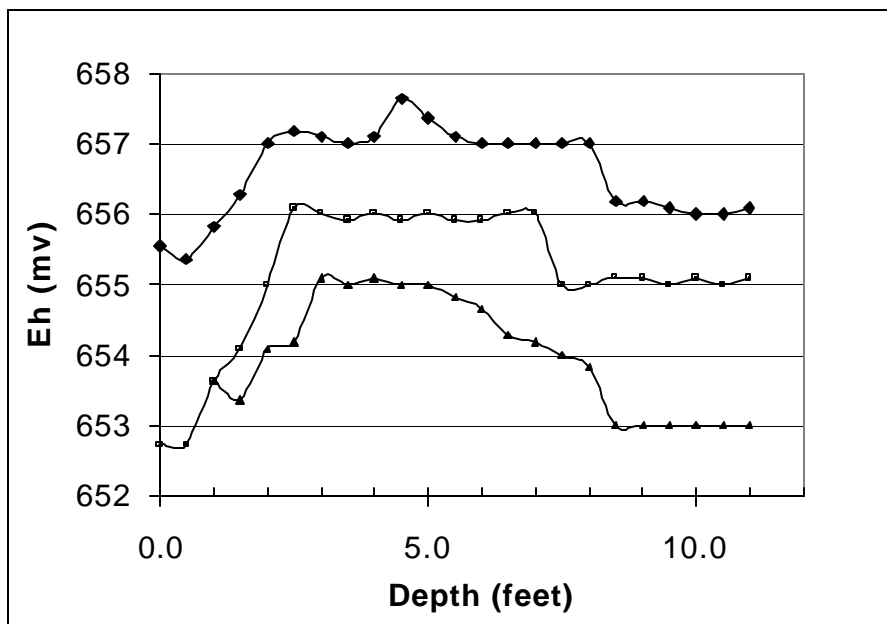
Figure 4-17. Typical effect of UV irradiation and atmospheric control on E_H as a function of depth (ft) in a 6-inch-diameter column of Berkeley Pit lake water as measured over a 3-week period.
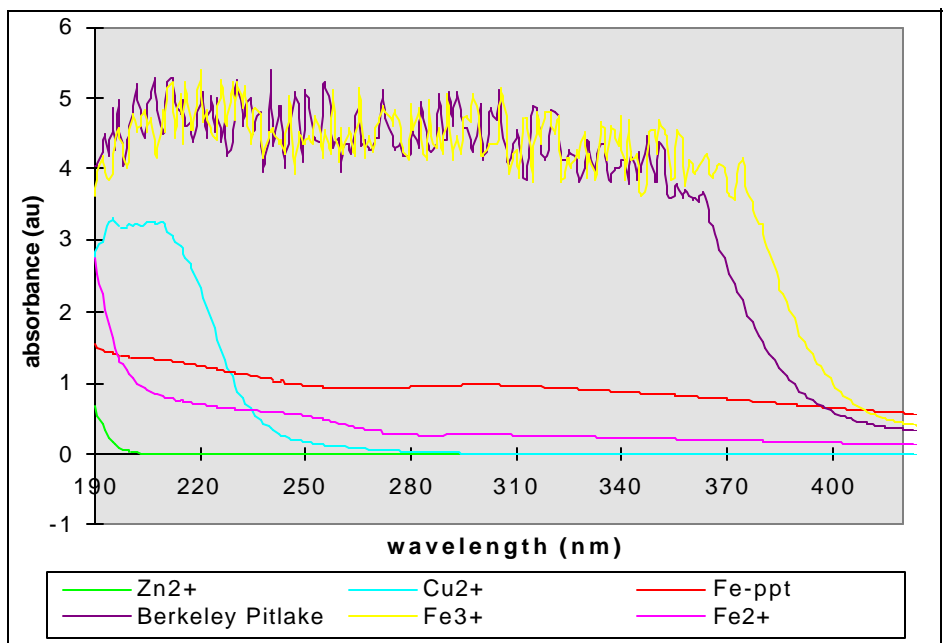
**Figure 4-18. Ultraviolet-vis absorbance spectra of dissolved metal sulfates at concentrations equivalent to Berkeley Pit lake water. Spectra are compared to surface Berkeley Pit lake water, a mixture of Berkeley Pit lake precipitate (presumably schwertmannite), and pure water.**

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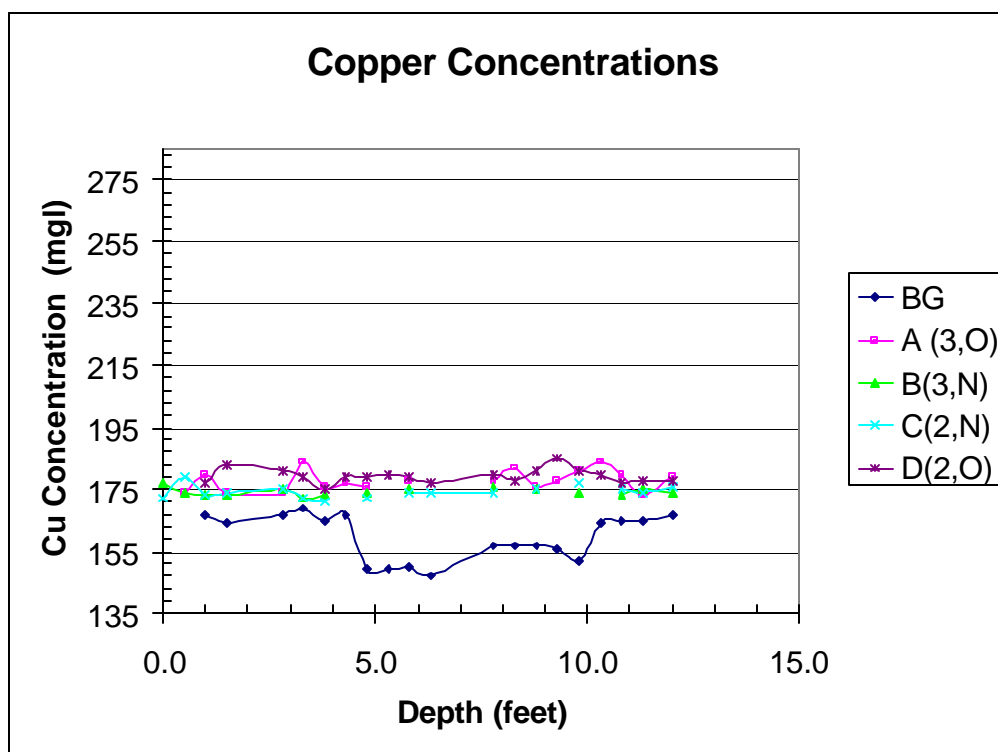
Figure 4-19. Copper concentrations Versus depth in 6-inch-diameter column.
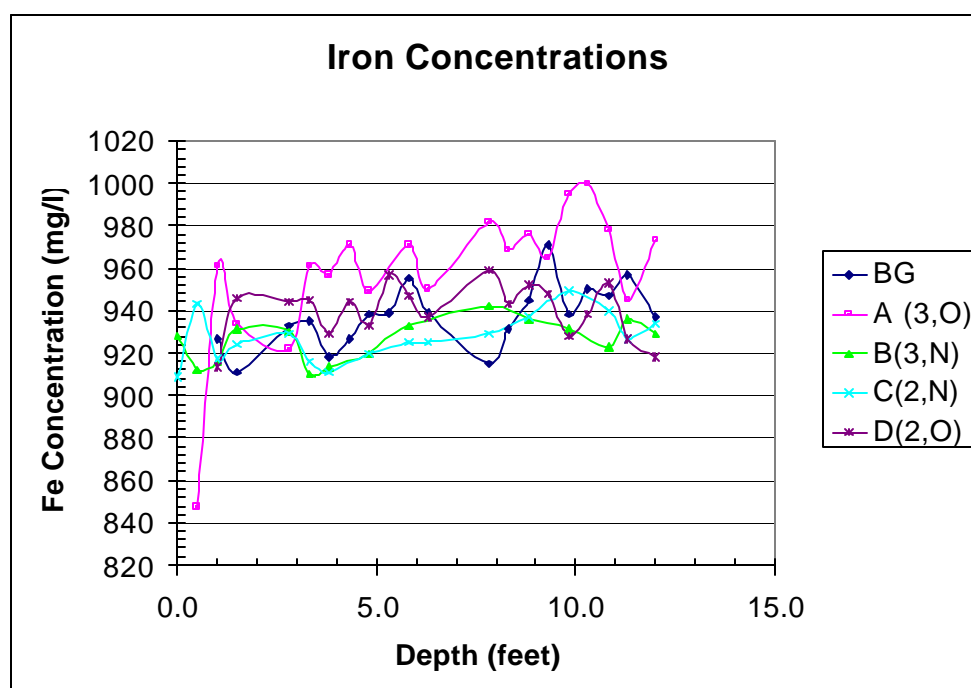
Figure 4-20. Iron concentrations versus depth in 6-inch-diameter columns.
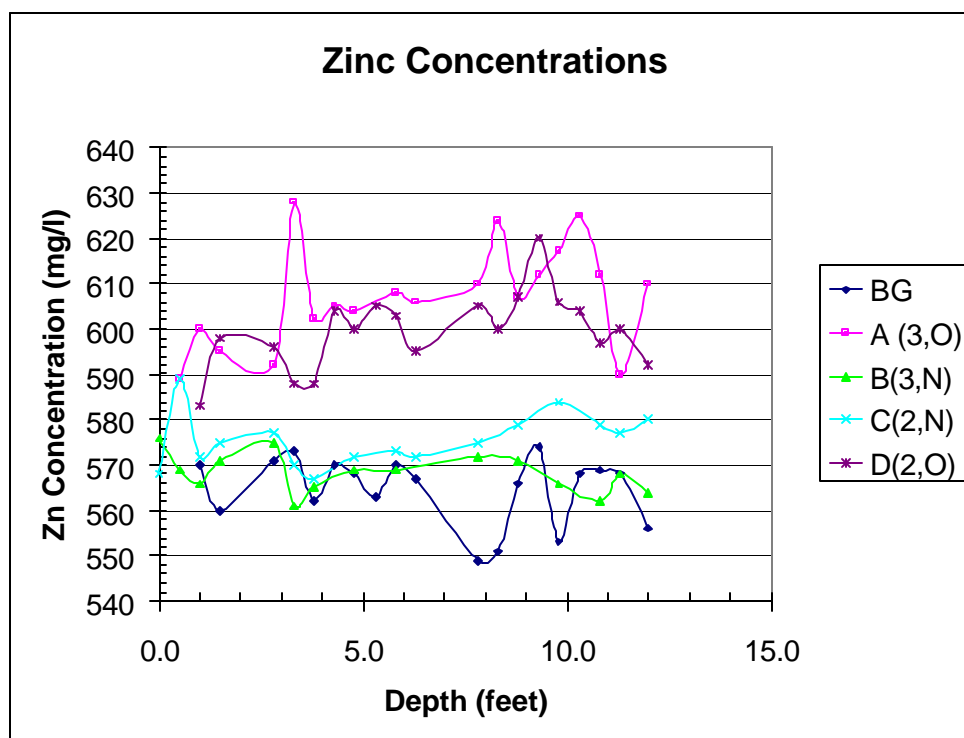
Figure 4-21. Zinc concentrations versus depth in 6-inch-diameter columns.

Table 4-1. Photolytic Conditions Used for Column Testing of Berkeley Pit Lake Water

Experiment	UV Wavelength	Gas Type
Background	NA	NA
Test A	365 nm	Compressed air
Test B	365 nm	Nitrogen
Test C	254 nm	Nitrogen
Test D	254 nm	Compressed air

5. Quality Assurance/Quality Control

The major objectives of this MWTP project were to identify photolytic processes, if any, that could be occurring naturally in the Berkeley Pit lake and, if so, assess whether the processes could be enhanced and used for the remediation of AMD waters. The programmatic and regulatory setting in which the project QA was conducted was Category IV, as outlined in Reference 36. Projects are designated Category IV when they are used to produce results for the purpose of assessing suppositions. Existing background data presented in Section 2 of this report was not required to conform to any criteria. This information is considered common knowledge since it was predominantly the foundation to the Work Plan (Ref. 59).

5.1 Quality Assurance/Quality Control Objectives

The QA/QC objectives outlined for the project were specified to generate acceptable data. The MWTP Activity VII, Project 4 QAPP (Ref. 36) was provided to ensure:

- measurements were appropriate for achieving project objectives;
- QC procedures were sufficient for obtaining data of known and adequate quality; and
- such data would be defensible if technically challenged.

With QA/QC objectives satisfied, project objectives had a more likely chance of being satisfied as well, but only as long as the data could be interpreted as such.

5.2 Analyses

Berkeley Pit lake test solutions were monitored for pH, DO, E_H, SC, turbidity, and the four highest metal concentrations of iron, zinc, aluminum, and copper. Only EPA-approved methods were employed for these measurements. Manufacturer specifications were followed as needed

particularly in regard to measuring temperature and depth.

5.2.1 Procedures

The EPA-approved methods (Refs. 60 and 61) included electrometric measurement (Method No. 4500) and inductively coupled plasma (ICP) spectroscopy (Method No. 6010A). Electrometric measurements were conducted simultaneously with a Hydrolab in the reaction vessel every week to determine pH, DO, E_H, temperature, conductivity, and turbidity. Inductively coupled plasma measurements were conducted off site by a reputable QA/QC laboratory to ascertain iron, zinc, aluminum, and copper concentrations. No control on any of the parameters was conducted. Equipment manufacturers and types are specified in Section 3.

5.2.2 Calibrations

Because up to 26 measurements were conducted continually through the length of the reaction vessel, modified procedures were needed so the contents of the vessel were not disturbed. Otherwise, recalibration procedures would have been done after every 20 measurements, and the Hydrolab would have been withdrawn and reinserted to do so; this would have been undesirable. Calibrations were made immediately before every weekly measurement.

pH: Buffer solutions at pH 1.0 and 4.0 were used in the standard two-point calibration of the pH meter. The buffer pH values bracketed the pH that was measured. Percent slopes were consistently found to be 100% $\pm$ 5%.

Specific Conductivity: Specific conductivity calibration was conducted using the two-point slope method. Solutions of potassium chloride measuring 1,413 and 9,948 micro-ohms per centimeter were used. The 1,413 solution was made in the lab following Standard Methods 2,510.

The 9,948 standard was purchased from Fisher Scientific.

Dissolved Oxygen: Dissolved oxygen was calibrated using percent saturation based on the barometric pressure reading from the ELC building. This reading is then internally converted to ppm by the Hydrolab probe. Before each sampling, the DO membrane was visually checked for wrinkles, bubbles, tears, or fouling. If any defections were found, the membrane and electrolyte were replaced. The membrane type is designed for low flow, i.e., nonflowing water.

Turbidity: Turbidity was also calibrated using the two-point method. Standards of 0.02 and 100 ntu are used to determine the turbidity of tap water, which is then used to calibrate the probe.

Redox Potential (E_H): The E_H was calibrated by dissolving quinhydrone in pH buffers of 4.0 and 7.0 at temperatures of 20 EC, 25 EC, and 30 EC respectively. Measurements were found to be accurate to within 2 mV. Because this was acceptable, no adjustments to the instrumentation were made.

Temperature/Depth: There is no field method to calibrate these two functions; both must be calibrated at the factory. The temperature sensor is built into the SC probe and requires no maintenance. Depth is determined from the pressure of the water above the probe port, which is located at the bottom of the probe. This calculation/conversion is done internally by strain gauge-type transducer.

Metal Concentrations: After samples were collected from the reaction vessel at the conclusion of each test, the samples were preserved in a 5% nitric acid matrix and stored in a refrigerator until sent to an outside laboratory for analysis. Samples were obtained through ports located on the sides of the reaction vessel. The samples were then passed through 0.45-Fm filters using disposable syringes purchased from Fisher

Scientific. Filters were used only once. Syringes were washed with dilute nitric acid and distilled water then dried for future use.

5.3 Field Samples

Berkeley Pit lake water measuring 25 gallons was collected three times per week and transported to the ELC Building by the MBMG. The water was obtained from the 200-foot depth, i.e., deep Berkeley Pit lake water. Seventeen gallons were placed immediately into the reaction vessel, and the remaining 8 gallons were stored in a refrigerator for future use and to help maintain freshness throughout an experiment. Once tests were completed, all 25 gallons of the sample were returned to the Berkeley Pit except for samples taken for analysis.

5.4 Quality Assurance/Quality Control Check Procedures and Activities

5.4.1 Check Procedures
Numerous procedures were in place to ensure quality data was reported. These check procedures included:

- recalibrating the various instruments used through the course of the tests as described in Section 4;
- analyzing calibration standards periodically to ensure the various instruments were functioning properly as described in Section 4;
- measuring reagent blanks periodically to make sure the various instruments were not contaminated, thereby giving false readings;
- matrix spiking a test to ensure the various instruments were functioning properly, thereby yielding results within 75% to 125% recovery; and
- verifying interelement, interference, and background correction factors for the ICP.

Only two of these QA/QC check procedures were found to fail. The latter three procedures were

conducted by the outside laboratory for measuring   the metal concentrations.

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